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HISTORY OF CHEMISTRY

IN

ANCIENT AND MEDIEVAL INDIA

INCORPORATING THE

History of Hindu Chemistry

by the Late ACHARYA PRAFULLA CHANDRA RAY

Edited by :

P. RAY

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The present volume furnishes an authoritative account of the chemical knowledge acquired by the Indians since the prehistoric days of the fourth millenium B. C. up to the end of the Moghul period or the advent of the British (circa 1800 A.D.). The contributions made by the Indians both to the speculative side and practical aspects of the subject has been recorded and discussed, as far as it has been possible, in a chronological order. Many new materials, besides those found in the History of Hindu Chemistry, have been added, and all materials have been carefully sifted so as to exclude what appear to be of doubtful origin or spurious character. Since the History of Hindu Chemistry by P. C. Ray has gone out of print more than 25 years ago, there has been no authentic and systematic account of the achievements of Indians of early and medieval ages in this field, available in any publication in the market. The present publication is therefore expected to remove a long felt want of the historians of science in general or of chemistry in particular. References have also been made to the social and cultural conditions of the country prevailing at each stage of development of the knowledge in respect of this particular branch of science. Definite evidences, supported by illustrations wherever possible, of the remarkable skill displayed by the ancient Indians in the art of making glazed pottery, in the extraction and working of metals and alloys, in the preparation of caustic alkalies, oxides and sulphides of metals, particularly of mercury, have been recorded. Students and historians of science, will find in this book ample materials of interest and value for the proper assessment of the ancient Indian civilization and culture. We annex here below the main contents of the book followed by a few selected excerpts.

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INTRODUCTION. I. Pre-Historic India. (c. 4000-1500 B.C.) :—Chapter I :—Pre-Harappan Period (c. 4000-2000 B.C.). Chapter II :—Indus Valley Civilization (c. 2500-1800 B.C.). Chapter III :—Post-Harappan Period (c. 1800-1500 B.C.).

II. Vedic and Ayurvedic Period (c. 1500 B.C.—800 A.D.) :—Chapter I :—Chemistry in the Vedas (c. 1500-600 B.C.). Chapter II :—The constitution and properties of matter. Atomic Theory. Chemistry in the Ayurvedic period. Chapter III :—Chemistry in Kautilya—Chemistry in Practical Arts (c. 600 B.C.—100 A.D.). Chapter IV :—Chemistry in Charaka and Susruta. Chapter V :—Chemistry in Bower Manuscript. Chapter VI :—Chemistry in Vagbhata. Chapter VII :—Chemistry in Practical Arts (A).

III. Transitional Period. (800-1100 A. D.). Chemistry in Vrinda and Chakrapani : Chapter I :—Vrinda (c. 800 A.D.) : Chapter II :—Chakrapani (c. 1060 A.D.).

IV. Tantric Period. (700-1300 A.D.) : Chapter I :—General Survey. Chapter II :—Chemistry in Rasaratnakara of Nagarjuna. Chapter III :—Chemistry in Rasarnava. Chapter IV :—Chemistry in Sarvasvararasayana. Chapter V :—Chemistry in Dhatuvada. Chapter VI :—Chemistry in Rasahridaya. Chapter VII :—Chemistry in Kakachandeswarimata Tantra. Chapter VIII :—Chemistry in Rasendrachudamani of Somadeva. Chapter IX :—Chemistry in Rasaprakasasudhakara of Yasodhara. Chapter X :—Chemistry in Rasachaintamani of Madanantadeva. Chapter XI :—Chemistry in Rasakalpa.

V. Iatro-Chemical Period. (1300-1600 A.D.) : Chapter I :—General Survey. Chapter II :—Chemistry in Rasaratna Samuchchaya. Chapter III :—Chemistry in Rasaraja-lakshimi.

Notes on the Minerals, gems, salts, etc.

CHEMISTRY IN PRACTICAL ARTS. (B) :—Chapter 1 :—Metallurgy and Working in Metals. Chapter 11 :—Gun-powder, Saltpetre, Mineral Acids, Alums etc. Chapter III :—Paper, Ink, Soap and Cosmetics, etc.

Decline of Scientific Spirit in India

APPENDIX A. The Mechanical, Physical and Chemical Theories of Ancient Hindus.

APPENDIX B. Tibetan Texts in Roman Scripts.

APPENDIX C. Sanskrit Texts in Devnagri Scripts.

The book contains a large number of Illustrations.

Dealing with the preparation and use of alkalies and alkaline caustics Susruta makes the following remarkable observations (*circa* 2nd century A.D. or even earlier) :

"Alkalies are of two sorts, namely, for external application and internal administration. They are made of three different strengths (in solution), namely weak, moderate and strong. Susruta describes the preparation of these three varieties of alkali.

"With due religious ceremonies some trees or plants are cut to pieces on an auspicious day in autumn by the workers. These pieces are piled in a place free from

wind. Some limestone should be placed on the pile and then set on fire by stalks of a selected plant. When the fire is extinguished, the ashes of the tree and the burnt lime should be kept separate.

"Thirty-two seers of ashes should be stirred or mixed with six times their quantity of water and the mixture strained through cloth. This should be repeated twenty-one times. The strained fluid should then be boiled slowly in a large pan and agitated with a ladle. When the fluid becomes clear, pungent and soapy to the feel, it should be removed from the fire and strained through cloth. The dregs being thrown away, the strained fluid should be again boiled. From this alkaline solution take three quarters of a seer.

"Then take eight palas each of burnt limestone, conch shells and bivalve shells, and heat them in an iron pan till they are of colour of fire. Then moisten them in the same vessel with the above mentioned three quarters of a seer of alkaline water and reduce them to powder. This powder should be thrown on sixty four seers of the alkaline water and boiled with constant and careful agitation by the ladle. Care should be taken that the solution is neither too thick nor thin.

"When reduced to proper consistence, the solution should be removed from fire and poured into an open jar. The opening or mouth of the jar should be covered and should be kept in a secluded place. This preparation is called *madhyama kshara* or alkaline caustic of middling strength.

"When the alkaline water is simply boiled to the proper consistence without the addition of burnt shells, etc. the preparation is called *mridu kshara* or mild alkaline solution.

"The strong alkaline caustic, i.e, *tikshna kshara*, is prepared by boiling the weak solution with some dried plants in the form of powder."

Obviously *tikshna kshara* represents concentrated caustic alkali solutions.

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[Jour. Indian Chem. Soc., Vol. 30, No. 4, 1953]

JOSHI EFFECT IN BENZENE VAPOUR UNDER X-RAYS. PART I. INFLUENCE OF EXCITING POTENTIAL

By G. V. Asolkar.

Joshi effect in benzene vapour under X-rays, in an ozoniser discharge, is studied due to 50 cycle potentials in the range 7—20 kV. The range of potential (V) studied consists of (*a*) 0—7.4 kV *i.e.* well below V_m, the 'threshold potential' (8 kV), the current being capacitative and unaffected by X-rays; (*b*) 7.4—7.95 kV where the discharge is not 'self maintained', a large reversible positive Joshi effect is observed; (*c*) a narrow region 7.95—7.68 kV characterised by an irreversible $+\Delta i$; (*d*) a region of 'self-maintained' discharge 8—20 kV where $-\%\Delta i$, maximum near V_m is observed. The results are explained by an extension of Joshi's theory associating $-\Delta i$ with the space charge effect due to negative ions, to a consideration of the behaviour of the positive ionic space charge

Arising out of Joshi's observation (*Curr. Sci.*, 1944, **13**, 278) of the producibility of a large negative Joshi effect ($-\Delta i$) in chlorine gas on exposure to X-rays, a powerful means of ionisation, its observation in other systems was investigated by a number of workers (Asolkar, *Proc. Ind. Sci. Cong.*, 1951, Part III, *Chem. Sec.*, Abs. No. 69, 70; Bhiday, *ibid.*, 1950, *Phys. Sec.*, Abs. No. 58; Bhide, *ibid.*, 1951, *Phys. Sec.*, Abs. No. 39, 40; Saxena and Karmalkar, *Curr. Sci.*, 1950, **19**, 276; Bhide, *ibid.*, 1951, **20**, 182). Non-occurrence of $\pm\Delta i$ in electrically excited benzene under both visible and ultraviolet suggested the desirability of the present extension of the preliminary work.

Experimental

Well purified benzene vapour in equilibrium with liquid phase at 27° corresponding to the pressure $p = 105$ mm. was excited by a 50 cycle transformer discharge in the annular space of Siemens' all glass ozoniser. The general experimental set up was similar to that developed by Joshi (*Benaras Hindu Univ. J.*, 1950). The discharge current i was measured with a mirror galvanometer actuated by RCA 30 triode used as a diode coupled resistively with the ozoniser. A radiator type Coolidge tube with a tungsten target was the source of X-rays. The voltage on the X-ray tube (anode voltage) was taken as a measure of the penetrating power of the radiation (Rutherford, Barnes and Richardson, *Phil. Mag.*, 1915, **30**, 339).

The anode current indicated the intensity of the radiation (Rutherford, *ibid.*, 1917, **34**, 201). The ozoniser was enclosed in a lead-lined chamber, with a lead shutter movable by a pulley. The ozoniser current i at a given exciting potential V, was measured when it was shielded from X-rays (i_D) and when exposed to it (i_L). The difference $i_D \sim i_L$ gave the net Joshi effect Δi and its relative value $100 \times \Delta i/i_D$, under X-rays of a given intensity I, in terms of tube current and hardness as anode voltage in kV. The wave form of the discharge current and its time delineation were observed, following Joshi's method (*Nature*, 1944, **154**, 147; *Curr. Sci.*, 1944, **13**, 253)

using a cathode ray oscillograph (208B Du Mont). The results for i_D, i_L, Δi and $\%\Delta i$ at the exciting potentials varied in the range 7 to 20 kV, for anode voltages 23.2 and 20.1 kV and tube current 3.0 mA are recorded in Tables I and II, in part expressed graphically in Figs. 1 and 2, in respect of a typical oscillographic record in Fig. 3 (a, b, c). It may be mentioned that out of the results for Joshi effect, using ozonisers of different spacings under varied operative conditions, only one group is now reported.

TABLE I

Variation of Joshi effect with exciting potential in benzene vapour under X-rays.

Below V_m. $pC_6H_6 = 105$ mm at 27°. Frequency of A. C. supply = 50 cyc./sec. Source of X-radiations = Coolidge tube. Intensity (tube current) = 3 0 mA.

Exciting potential.	Anode voltage = 23.2 kV.				Anode voltage = 20.1 kV.			
	i_D.	i_L.	Δi.	$\%\Delta i$.	i_D.	i_L.	Δi.	$\%\Delta i$.
7.44 kV	3	3	0	0	3	3	0	0
7.50	4	8	+ 4	+100	4	7	+ 3	+ 75
7.56	5	18	+13	+216	5	16	+11	+220
7.62	6	26	+20	+333	6	24	+18	+300
7.68	6	27	+21	+350	7	27	+20	+285
7.74	7	28	+21	+300	7	26	+19	+271
7.80	8	29	+21	+262	8	27	+19	+237
7.86	9	29	+20	+222	9	28	+19	+211
7.92	12	30	+18	+150	12	28	+16	+133
7.98	25	31	+ 6 (irreversible)	+ 24	25	29	+ 4	+ 16
8.04	50	34	−16	− 32	50	36	−14	− 28
8.10	72	52	−20	−27.7	—	—	—	—

TABLE II

Variation of Joshi effect with exciting potential in benzene vapour under X-rays.

Above V_m. Other conditions same as in Table I.

Excitng potential.	Anode voltage = 23.2 kV.				Anode voltage = 20.1 kV.			
	i_D.	i_L.	$-\Delta i$	$-\%\Delta i$	i_D.	i_L.	$-\Delta i$	$-\%\Delta i$
8.0 kV	75	52	23	30.6	75	54	21	28
9.0	95	70	25	26.3	95	72	23	24.2
10.0	115	88	27	23.5	115	91	24	20.8
11.0	135	106	29	21.5	135	110	25	18.5
12.0	160	129	31	19.4	160	133	27	16.9
13.0	174	143	31	17.7	174	147	27	15.5
14.0	200	168	32	16.0	200	172	28	14.0
15.0	216	184	32	14.8	216	187	29	13 4
16.0	230	118	32	14.2	230	200	30	13.0
17.0	254	222	32	12 8	254	226	28	11.1
18.0	265	232	33	12.4	265	235	30	11.1
19.0	295	259	36	12.2	295	263	32	10.8
20.0	325	286	39	11.8	325	290	35	10.7

Discussion

The foregoing results show the occurrence of both positive and negative Joshi effect in excited benzene vapour when exposed to X-rays. As is to be expected from general photochemical considerations, the magnitude of the effect is influenced markedly by the hardness and intensity of the radiations.

It is interesting to observe from Table I, the occurrence of a large *reversible* positive effect, e.g. + 350% at 7.68 kV, decreasing to + 150% at 7.92 kV under 23.2 kV X-rays; while the corresponding values for 20.1 kV X-rays are + 285% and + 133%, *i.e.* an increase of conductivity by X-radiation at voltages just less than V_m; the more familiar and apparently anticonventional negative effect $-\%\Delta i$ is maximum near V_m and decreases numerically at larger V, e.g. the results show -30.6% at 8.0 kV decreasing numerically to -11.8% at 20.0 kV (see Table II and Fig. 2) for anode voltage 23.2 kV. The corresponding values for 20.1 kV X-rays are -28.0% and -10.7%. Fundamentally similar results were first observed by Joshi in iodine vapour in the visible range (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, *Chem. Sec.*, p. 70). and subsequently by others in various systems (Mohanty and Kamath, this *Journal*, 1948, **25**, 405; 1949, **26**, 553; Deshmukh, *ibid.*, 1947, **24**, 211; Shukla, *J. Phys. Coll. Chem.*, 1949, **53**, 1239; Joshi, *B.H.U. Jour.*, 1950) *.

In all forms of discharge, especially the point to plate, the wire in cylinder, and the full ozoniser, a consideration of the current-voltage characteristics of which curves in Fig. 1 are typical, is necessary for the understanding of the discharge mechanism and the associated *Joshi effect*. In agreement with Joshi (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 29, 389) it was observed that irradiation even with the most intense available and very penetrating X-radiations produced no Joshi effect at applied potentials well below V_m, *i.e.* when the current is entirely capacitative and is given by $2\pi nCV$, where n is the supply frequency, C, the distributed capacity and V, the exciting potential. This represents the initial flat section of the V—i characteristic.

Towards the end of the flat region the oscillograph shows chiefly a distortion due presumably to some of the higher harmonics setting in along with the fundamental frequency. As the voltage is increased the galvanometer (of period t = 12 sec.) shows intermittent fluctuations. A glow then sets in, which is initially markedly unsteady and flickering; it subsequently gains in intensity. At this stage the cathode ray oscillograph shows the inception of high frequency pulses and the corresponding current i increases rapidly. The gas now breaks dielectrically and a conduction current associated with the discharge sets in. This is the region designated as the 'threshold' V_m by Joshi (*Trans. Faraday Soc.*, 1929, **25**, 118, 137) and shown by him to be of fundamental im

* It is extremely likely that $+\Delta i$ arises substantially from the photoelectric ionisation by the X-rays The precipitous inversion of $+\Delta i$ into $-\Delta i$ beyond V_m; former's occurrence at both small and large V and of $-\Delta i$ at intermediate V, the appreciable decrease of $+\Delta i$, ending under certain conditions, with change to $-\Delta i$, as the intensity and frequency of irradiation are increased progressively in both the X-ray and the visible regions; the much greater temperature sensitivity of $+\Delta i$ than that generally known for the photoelectric effect, as also the results of the favourable influence of increased supply frequency and the presence of polyatomicals suggest that $+\Delta i$ may not be identified at the present stage with the classical photoelectric effect.

portance in the production of $-\Delta i$ (Joshi, *Curr. Sci.*, 1939, **8**, 548) and indeed of any discharge reaction of a chemical and physical type. Further increase of voltage by even a slight extent augments appreciably the current i which becomes more stable and

FIG. 1

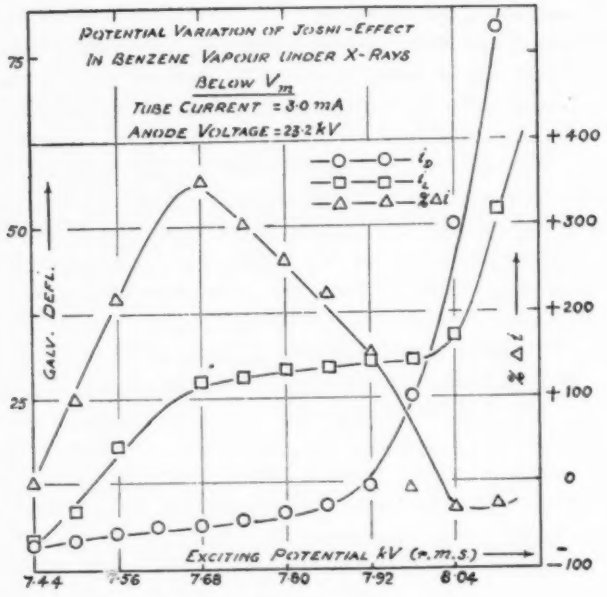
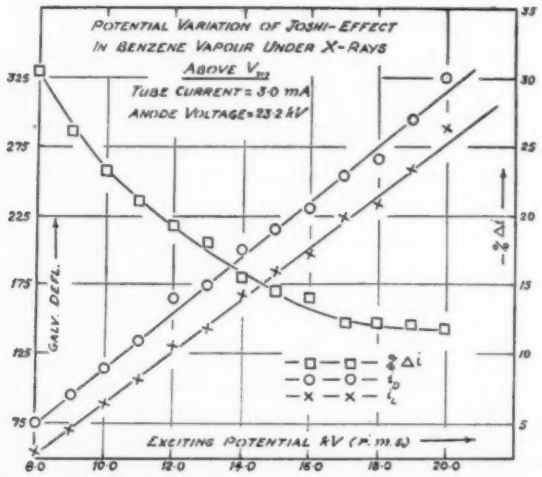


FIG. 2



richer in high frequencies (h.f.'s). The glow also tends to be more uniform and luminous though comparatively concentrated near the inner electrode where the field is strongest.

Joshi has shown the dependence of Δi on a number of operative conditions such as the gas pressure, temperature, nature of the elecrtode surface, supply frequency, 'ageing' under discharge etc., and that the discharge current i depends on the overvoltage $(V-V_m)$ (Joshi, *Trans. Faraday Soc.*, 1927, **23**, 227).

The present series of experiments (under X-rays) have confirmed Joshi's finding of the appearance of the h.f.s at V_m, and especially, the general result with visible light that the $-\%\Delta i$ is maximum near V_m, being linked preferentially with the suppression of these h.f.s (Joshi, *Nature*, 1945, **154**, 147; *Curr. Sci.*, 1945, **14**, 67) and that it declines with much larger V.

It must be emphasised at this stage that $\pm \Delta i$ under X-rays are practically instantaneous and light reversible as in the visible, the last implies that in e.g., $-\Delta i$, the reduction of the current as observed on the galvanometer and of the h.f. amplitude as shown by the cathode ray oscillograph, are restored instantaneously on screening off the radiation. In the positive effect produced just below V_m region, the increase in the current and of the h.f. amplitude produced by radiations revert to the previous low values in dark on shutting it off. In this connection it is interesting to record what may be called 'irreversible positive effect' (Marathe and Bommannavar, *Nature*, 1950, **168**, 890). This was observed at 7.98 kV with X-rays of hardness and intensity corresponding to 23.2 kV and 3.0 mA respectively (see Table 1). It was now observed that the increased current $+\Delta i$ and h.f. pulses produced by radiation persisted even on shutting off the X-rays, indicative of some inertial hysteresis-like effect.

Joshi's theory (*Curr. Sci.*, 1947, **16**, 19) of this phenomenon postulates: (*a*) formation of an adsorption-like electrode layer consisting of ions and excited particles derived from the discharge space and possessing a low work function; (*b*) irradiation of the system causes emission of electrons from (*a*); (*c*) the negative Joshi effect $-\Delta i$ is a space charge effect due to negative ion formation from *inter alia* the photo-electrons from (*a*) due to capture by the particles in the discharge space owing to their increased 'electron affinity' by excitation. This theory explains the wide occurrence of $-\Delta i$ in electronegative gases, the pronounced influence of 'ageing' and electrode surface condition, and the fact that both at high temperatures and high voltages $-\Delta i$ is reduced due to the adsorption-like layer being impaired by strong heating and intense ionic bombardment at a very large potential, V. Under moderate conditions of gas pressure (p) and applied V, the general result that $-\Delta i$ increases with p/X is explained since p/X determines the probability of electron capture leading to negative ion formation. Joshi (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 389) has emphasised that $-\Delta i$ is maximum near V_m where the chemical effect of the discharge reaction is minimum. It is, however, extremely likely that even at these low voltages benzene decomposes slightly to give especially at early stages such products as hydrogen, ethane and like unsaturated hydrocarbons (Deshpande, unpublished results) and especially free radicals; these last account for the formation under discharge of such products as diphenyl (Deshpande, *loc. cit.*). These free radicals have a high electron affinity and are favourable therefore for the negative ionic space charge leading to appreciable $-\Delta i$, as observed. It also follows from Joshi's theory that since low V disfavours electron capture in (*c*), the photoelectrons from (*b*) and the cumulative

ionisation by their movement under V should give the positive effect, as actually observed to be a characteristic of low voltage excitation.

It is now suggested that the space charge effect causing $\pm\Delta i$ can originate from the behaviour of the positive ions also, besides negative ions in the general mechanism presented by postulates (*a*) and (*b*) in Joshi's theory. It is instructive to consider in this connection the analogy which obtains between an ozoniser discharge and the widely studied point to plane corona (Loeb, *Phys. Rev.*, 1941, **60**, 714; 1947, **71**, 712; Trichel, *ibid.*, 1938, **54**, 1078; 1939, **55**, 382; Kip, *ibid.*, 1939, **55**, 549) and especially the coaxial cylinders and Geiger Muller counter (Werner, *Z. Physik*, 1934, **90**, 394; 1934, **92**, 702; Wilknison, "Ionisation Chambers and Counters", Cambridge Univ. Press, 1950; Korff, "Electron and nuclear counters", D. Van Nostrand Co., New York, 1949).

The points of difference between the counter and Siemens' type ozoniser are:

(*i*) Radius of the inner electrode wire r_1 is very small in the former than in the ozoniser. Consequently the region of intense ionisation limited by the critical radius r_0 is very near the wire of a counter, while in the ozoniser r_0 is extended in the gap and the region of intense ionisation is comparatively near the outer cylindrical cathode. The field gradient in the ozoniser for the same reasons does not show such extreme inhomogeneity as in the counter.

(*ii*) In the counter metal electrodes are employed, whereas in the ozoniser both electrodes are of glass. This does not materially alter the discharge mechanism as Maze (*J. Phys.*, 1948, **7**, 164) has used the counter consisting of soda glass cathode showing similar characteristics as metal ones.

By an analogy with the counter, the possible origin of the current pulses occurring in an ozoniser becomes clear. In both these, the intense field region is characterised by a large amplification at the inner electrode. An occasional electron will have an increasing drift velocity and later causes Townsend avalanches leaving behind a space charge of positive ions during the period the central electrode is positive [the essential argument is not affected materially (Wilkinson, *loc. cit.*, p. 120) by considering the reversed polarity]. This positive space charge reduces the field near the anode, inhibiting initially the growth of the avalanches and finally choking them off completely. Such a mechanism gives rise to relaxation oscillator-like pulses as shown in Fig. 3 a The h.f. pulses in the ozoniser (Fig. 3b), observed with a higher writing speed of a C.R.O., show an unmistakable resemblance with the Trichel pulses observed in the corona (Trichel, *loc. cit.*). The exceedingly rapid collection of electrons, yielding a charge Q during the active time 't_a' (of the order. 10^{-8} sec.), gives rise to the almost vertical streak, followed by the less inclined curve during its decline representing the comparatively slow movement of the positive ionic space charge during the traversal time, 't_m' (of the order 10^{-5} sec.). The positive ions during 't_m' gain energy enough to extract a secondary electron from the cathode; this electron in its turn will produce Townsend avalanches and the process repeats itself giving rise to a succession of pulses causing a self-maintained discharge.

The fundamental role of V_m may now be considered. V_m is envisaged as that potential, at which the positive ions being residual from previous Townsend avalanches eject a cathodic electron and make the discharge self-maintained. Since the ejection from

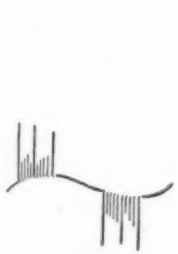


FIG. 3(*a*)

FIG. 3(*b*)

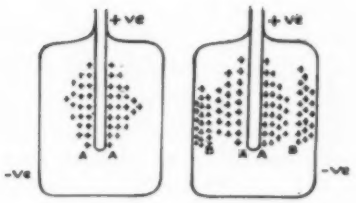


FIG. 3(*c*)

the cathode is a statistical process, it is to be anticipated that V_m, initiating the region of self-maintained discharge, is not sharp but distributed over a narrow potential region, as observed.

Montgomerys have argued (*Phys. Rev.*, 1940, **57**, 1030) that the current i in such discharges is expressed by Q/t_m to a first approximation, where Q is the charge collected during 't_a' and 't_m' is the relaxation time (neglecting 't_a' in comparison to 't_m' in the denominator). The effect of irradiation may now be considered in two stages during 't_a' and 't_m' responsible for the mechanism of the pulse.

Irradiation during the Active Time 't_a'.—During the growth of the normal pulse and the building up of the initial positive space charge to its full choking concentration, a certain photoelectron ejected on irradiation is able to ionise cumulatively in the region between the cathode and r_c leaving its space charge $[B]$ (see Fig. 3*c*). This is possible due to the enhanced field $(X+X_1)$ where X is the field due to the applied voltage, and X_1 due to initial positive space charge $[A]$. The additional space charge $[B]$ reduces the field near the anode, further decreasing α, Townsend's first coefficient (for ionisation by collision) below its value in dark. Due to this reduction in α under irradiation the charge collected by the anode is $Q_1 < Q$ (in dark).

This accounts for the decrease in amplitude under irradiation leading to $-\Delta i$. Further, the additional space charge $[B]$ produced on irradiation has a screening effect on the initial space charge $[A]$, thereby increasing its 't_m'. Thus, irradiation causes a decrease in Q during 't_a' and a consequent increase in 't_m'. Both these contribute to a decrease in the current yielding negative Joshi effect.

Irradiation during 't_m'.—At the end of the active time 't_a' the space charge $[A]$ begins to move to the cathode under an enhanced field $(X+X_1)$. Photoelectrons ejected during this time move through this enhanced field near the cathode and produce ionisation by collision between the space charge $[A]$ and the cathode. This increases 't_m', and hence leads to a decrease in amplitude and the current, *i. e.* yields $-\Delta i$. The increased ionisation also results in the production of "spurious pulses" or pulses of not normal amplitude yielding a simultaneous opposite component $(+\Delta i)$ of the net negative Joshi effect. The ionisation of the gas by X-rays also increases the probability of the occurrence of the component $(+\Delta i)$. This is supported by the findings of Fenton and Fuller (*Proc. Phys. Soc.*, 1949, **62**, 32) that the probability for the occurrence of spurious pulses is accurately proportional to the charge generated in the dis-

charge. This co-occurrence of $\pm\Delta i$ was observed directly first by Joshi (*Proc. Indian Sci. Cong.*, 1947, *Phys. Sec.*, Abs. No. 25) and recently by Jatar in iodine vapour (*J. Sci. Ind. Res.*, 1950, **9B**, 283). It may also be mentioned that Loeb *et al.* (*Phys. Rev.*, 1941, **60**, 714) noticed in a point to plane discharge that irradiation with the ultraviolet caused either of two simultaneous and opposite components $\pm\Delta i$ to predominate. A suggestive analogue of the co-occurrence of $\pm\Delta i$ has been observed by Bhiday, Bhide and Asolkar (*Proc. Indian Sci. Cong.*, 1950, Part III, *Phy. Sec.*, Abs. No. 61) in the action of the magnetic field on the discharge current i in excited Hg vapour.

Positive Joshi effect.—As can be seen from Table I and Fig. 1, this positive effect persists only over a narrow potential range below V_m (viz. 7.95 – 7.98 kV). The discharge in this region is 'non-self-maintained' *i.e.* the field $(X+X_1)$ acting on the ionic space charge is insufficient to give enough energy to the positive ions to extract an electron from the cathode. This can be achieved at the same X, by increasing the ionic concentration resulting in larger X_1 (obtained by the action of light, in this case by X-rays) supplying trigger electrons from postulate (*a*) in Joshi's theory. The discharge then starts yielding a large pulse height due to an increase in Q. Under irradiation the discharge becomes self-maintained (due to increased concentration of positive ions). But as soon as the irradiation is stopped, the ozoniser current returns to its original position on $V-i$ curve before irradiation. Thus, for the potential region just below V_m ionisation is caused by X-ray photons resulting in the increase of i. The mechanism postulated above finds further support in the experimental observation of Arnikar and Naqvi (*Proc. Indian Sci. Cong.*, 1951, Part III, *Phys. Sec.*, Abs. No. 20) viz. the large positive effect obtained in the visible range with argon-methane filled G. M. counter below V_m. The positive effect persists only over a narrow potential range below V_m. On crossing the V_m the discharge is rendered self-maintained and it is only when the discharge is continuous that the negative Joshi effect can be produced. V_m may also be characterised as the potential at which the positive effect changes to the negative effect.

The Variation of $-\%\Delta i$ *with Applied Potential.*—Increase of V enhances the concentration of the initial space charge $[A]$, photoelectronic yield is constant for a particular beam intensity and the additional space charge $[B]$ due to it may therefore be assumed constant throughout the voltage range above V_m to a first approximation. It follows from the above mechanism that the relative concentration of the space charges, (B/A), under irradiation should have the maximum value near V_m and that it should fall with increasing V since A increases in dark with V, and B is approximately constant. This therefore satisfactorily accounts for maximum $-\%\Delta i$ near V_m and its gradual decrease thereafter.

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JOSHI EFFECT IN BENZENE VAPOUR UNDER X-RAYS. PART II. INFLUENCE OF INTENSITY AND FREQUENCY

By G. V. Asolkar

The influence of fourteen-fold intensity (I) variation at a constant frequency (anode voltage), and at a constant intensity of a three-fold variation of frequency (ν_m) on Joshi effect, Δi, at a given exciting potential (V) is studied in (p = 105 mm.) benzene at 27°, excited by 8-16 kV (r. m. s.) of 50~. At constant V, with the progressive increase of I, $-\%\Delta i$ increases numerically almost linearly in the low I region, reaches a maximum at a critical I and *decreases* thereafter ; and *even changes sign at large I*, a tendency favoured by a large V and low anode voltage. At constant I, $-\%\Delta i$ (as also $-\Delta i$) increases with the increasing frequency of X-rays.

The results are explained from the standpoint of the choking action of the positive ionic space charge. The relation $i = Q/t_a + t_m$, where Q is the charge during $(t_a + t_m)$, t_a, the active time and t_m, the traversal time of the positive ions, is examined for the intensity and frequency variation of the X-radiation.

Data for the influence of intensity and especially frequency (*vide infra*) are of fundamental importance not only as quantitative determining factors of any light reaction, but to the elucidation of its mechanism. In the visible and also ultraviolet regions the difficulty of ensuring an independent and comparable intensity in widely separated frequency bands is well known. This limitation does not obtain appreciably in the case of X-radiations, yielded by a heated filament type emitter. Production of $\pm\Delta i$ (Part I, Asolkar, this *issue*, p. 233) in a typical organic compound like benzene vapour has more than an ordinary interest, as a hitherto unobserved fact. It was considered desirable therefore to study in some detail its variation over a wide range of intensity and frequency of incident radiation.

Experimental

The general experimental procedure for the observation of Δi under X-rays in benzene vapour (p = 105 mm. at 27°) has been described earlier (Asolkar, *loc. cit.*). The Coolidge tube employed as a source of X-rays allowed of a variation of its tube current (anode current) from 0-7 mA ; this current is considered a reasonably accurate measure of the intensity (I) of X-rays (cf. Part I, *loc. cit.*). The anode voltage is expressed in kilovolts (r. m. s.). It is known that at a given voltage and tube current X-rays of various frequencies and intensities are produced and that the frequency position of maximum intensity is related simply to the anode voltage. The influence of X-ray frequency on the magnitude of Δi at a constant intensity was restricted to observation of its dependence on anode voltage as a first approximation (Rutherford, Barnes and Richardson, *Phil. Mag.*, 1915, **30**, 339). This frequency (ν_m) as denoted by the anode voltage was varied from 10.8 to 26.3 kilovolts in steps of 3.1 kilovolts. The ozoniser charged with benzene vapour was excited over a fairly wide potential range. This exciting potential is denoted by kV (r. m. s.). The temperature of the system was maintained

constant within $\pm 3°$ at 27°. This is a necessary precaution in view of the generally observed sensitivity of $\triangle i$ to the temperature variation (Joshi and Deo, *Nature*, 1944, **153**, 434 ; Mohanty, this *Journal*, 1948, **25**, 557 ; Deshmukh and Sirsikar, *J. Amer. Chem. Soc.*, 1948, **70**, 3924 ; Bhide, *Proc. Indian Sci. Cong.*, 1951, *Phy. Sec.*, Abs. No. 40). It is known that an 'agening' effect is produced due to both (*a*) the discharge in absence of external radiation (Deo, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 76 ; Mallikarjunappa, this *Journal*, 1948, **25**, 197 ; Deshmukh, *ibid.*, 1949, **26**, 176) and (*b*) exposure to X-rays (Joshi, *Curr. Sci.*, 1944, **13**, 278) which affect sensibly the magnitude of $\triangle i$. This was minimised by limiting the former period to less than half a minute and that for X-rays to five seconds. In a given series of V—*i* characteristics the total amount of exposure seldom exceeded eight minutes and one minute in the two periods respectively. Further, the value of $\triangle i$ at the end of a given series agrees within $\pm 1\%$ to that at the commencement of the series indicating that any variation due to either type of 'ageing' is inappreciable. These results are recorded in Tables I, II and III, in part shown graphically in Figs. 1 and 2. Only a representative set of observations is shown, out of the results using ozonisers of different electrode spacings under widely varied operative conditions.

Discussion

Tables I-II and Fig. 1 show that $-\%\triangle i$ under X-rays increases with increasing intensity in the low intensity region. Thus, e. g., it rises from 1.3 to 14.6 for intensity variation from 0.1 mA to 1.5 mA tube current at a frequency corresponding to 10.8 kilovolts and 8.0 kV exciting potential. At a higher frequency such as 23.2 kilovolts the $-\%\triangle i$ shows the increase from 6.6 at 0.1 mA to 30.0 at 1.5 mA. Further increase in intensity yields a peak value for $-\%\triangle i$ between the intensity 2.0 mA and 2.5 mA. Thus, the peak values for 10.8 and 23.2 kilovolts X-rays are respectively -16.6% at 2.0 mA and -34% at 2.5 mA respectively. As the intensity is further increased $-\%\triangle i$ decreases slowly. Thus, between the intensities 3.0 and 7.0 mA the $-\%\triangle i$ decreased from 30.6 to 16.0 and from 14.0 to 2.0 for 23.2 and 10.8 kilovolts X-rays respectively at the exciting potential 8.0 kV.

For lower exciting voltage (e.g., 8 kV) and the frequency of X-rays corresponding to 10.8 kilovolts, the maximum $-\%\triangle i$ is 16.6 at 2 mA decreasing to -2.0% at 7.0 mA without changing sign. For higher values of V (such as 20.0 kV) and 23.2 kilovolts X-rays, the $-\%\triangle i$ rises from 1 to a maximum of 12.8 and decreases to 2.6 at 7 mA. In the X-ray region, the $-\%\triangle i$ at first increases rapidly with intensity, reaches a peak value and decreases slowly ; for large V and at very high values of *I*, it changes sign yielding $+\triangle i$ (Table II and Fig. 1). Thus, for anode voltage 10.8 kilovolts, and exciting potential 20.0 kV, $-\%\Delta i$ increases from 0.3 to a peak value 3.0 for anode current 2.5 mA slowly decreasing to 0.6 at 5.5 mA changes sign at 6.0 mA (Table II) yielding $+0.3$ $\%\triangle i$. Further increase in intensity to 7 mA anode current increases $\%\triangle i$ to $+1$. This inversion of $-\triangle i$ to $+\triangle i$ with intensity in the X-ray region is significant. This tendency is favoured by large *I*, and especially at large V and low anode voltage.

Extensive studies of the variation of $\triangle i$ with light intensities in the various frequency bands have been made (Joshi *B. H. U. Jour*, 1943, **8**, 99; Joshi and Deo,

TABLE I

TABLE I

Influence of intensity of X-rays on the Joshi effect in benzene vapour at different frequencies and constant exciting pontential.

$p C_6H_6 = 105$ mm. at 27°. Frequency of A.C. supply = 50 ~. Source of X-radiations = Coolidge tube.

Frequency (anode-voltage in kilovolts).		Intensity (anode-current in mA). 0.1	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
		Exciting potential = 8.0 kV (r.m.s.) Current in dark (i_D) = 150 (arbitrary units).														
10.8	i_L	148	140	133	128	125	127	129	133	136	139	141	143	145	146	147
	$-\Delta i$	2	10	17	22	25	23	21	17	14	11	9	7	5	4	3
	$-\%\Delta i$	1.3	6.6	11.3	14.6	16.6	15.3	14.0	11.3	9.3	7.3	6.0	4.7	3.3	2.6	2.0
13.9	i_L	145	136	127	121	116	117	120	123	127	130	132	134	136	138	139
	$-\Delta i$	5	14	23	29	34	33	30	27	23	20	18	16	14	12	11
	$-\%\Delta i$	3.3	9.3	15.3	19.3	22.6	22.6	20.0	18.0	15.3	13.3	12.0	10.6	9.3	8.0	7.3
17.0	i_L	144	133	124	118	112	111	112	115	119	122	125	128	131	132	134
	$-\Delta i$	6	17	26	32	38	39	38	35	31	28	25	22	19	18	16
	$-\%\Delta i$	4.0	11.3	17.3	21.3	25.3	26.0	25.3	23.3	20.6	18.7	16.6	14.6	12.6	12.0	10.7
20.1	i_L	143	131	121	114	109	105	107	111	115	118	121	123	125	128	130
	$-\Delta i$	7	19	29	36	41	45	43	39	35	32	29	27	25	22	20
	$-\%\Delta i$	4.6	12.6	19.3	24.0	27.3	30.0	28.3	26.0	23.3	21.3	19 3	18.0	16.3	14.7	13.3
23.2	i_L	140	128	119	111	105	99	104	108	112	115	118	120	123	125	126
	$-\Delta i$	10	22	31	39	45	51	46	42	38	35	32	30	27	25	24
	$-\%\Delta i$	6.6	14.7	20.7	26.0	30.0	34.0	30.6	28.0	25.3	23.3	21.3	20.0	18.0	16.7	16.0
		Exciting potential = 20 kV (r.m.s.). i_D = 650.														
20.1	i_L	645	625	608	594	581	576	584	593	602	610	617	624	629	633	636
	$-\Delta i$	5	25	42	56	69	74	66	57	48	40	33	26	21	17	14
	$-\%\Delta i$	0.8	3.8	6.5	8.6	10.6	11.4	10.0	8.7	7.4	6.2	5.0	4.0	3.2	2.6	2.2
23.2	i_L	643	621	602	584	572	567	573	582	593	601	609	615	623	628	633
	$-\Delta i$	7	29	48	66	78	83	77	68	57	49	41	35	27	22	17
	$-\%\Delta i$	1.0	4.4	7.5	10.1	12.0	12.8	11.8	10.2	8.8	7.5	6.3	5.4	4.2	3.4	2.6

TABLE II

Influence of intensity of X-rays on the Joshi effect in benzene vapour at different exciting potentials and constant frequency (anode voltage = 10.8 kilovolts).

pC_6H_6 = 105 mm. at 27° Frequency of A. C. supply = 50 ~. Source of X-radiations = Coolidge tube.

Exciting potential in kV (r.m.s.).			Intensity (anode-current) in mA. 0.1	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0
8	Current in dark i_D. 150(units).	i_L	148	140	133	128	125	127	129	133	136	139	141	143	145	146	147
		Δi	2	10	17	22	25	23	21	17	14	11	9	7	5	4	3
		$-\%\Delta i$	1.3	6.6	11.3	14.6	16.6	15.3	14.0	11.3	9.3	7.3	6.0	4.7	3.3	2.6	2.0
10	230	i_L	227	221	213	208	204	207	212	215	218	220	222	224	225	226	227
		Δi	3	9	17	22	26	23	18	15	12	10	8	6	5	4	3
		$-\%\Delta i$	1.3	3.9	7.4	9.5	11.3	10.0	7.8	6.5	5.2	4.3	3.5	2.6	2.1	1.7	1.3
12	320	i_L	318	312	308	304	301	302	305	307	310	313	315	317	318	318	319
		Δi	2	8	12	16	19	18	15	13	10	7	5	3	2	2	1
		$-\%\Delta i$	0.6	2.5	3.8	5.0	5.9	5.6	4.7	4.0	3.1	2.2	1.5	0.9	0.6	0.6	0.3
14	400	i_L	398	392	387	384	381	382	385	388	390	393	395	397	398	398	399
		Δi	2	8	13	16	19	18	15	12	10	7	5	3	2	2	1
		$-\%\Delta i$	0.5	2.0	3.2	4.0	4.8	4.5	3.7	3.0	2.5	1.8	1.2	0.8	0.5	0.5	0.2
16	450	i_L	448	444	438	435	432	434	438	442	444	445	446	447	448	449	450
		Δi	2	6	12	15	18	16	12	8	6	5	4	3	2	1	0
		$-\%\Delta i$	0.4	1.3	2.6	3.3	4.0	3.3	2.7	1.7	1 3	1.1	0.9	0.6	0.4	0.2	0
18	530	i_L	529	524	516	512	509	511	515	518	521	525	526	528	530	531	533
		Δi	1	−6	14	18	21	19	15	12	9	5	4	2	0	+1	+3
		$\%\Delta i$	0.2	1 1	2.6	3.4	4.0	3.6	2.8	2.2	1.7	1.0	0.7	0.4	0.0	+0.2	+0.6
20	650	i_L	648	641	632	628	625	626	630	635	639	647	646	649	652	655	657 0
		$-\Delta i$	2	9	18	22	25	24	20	15	11	7	4	1.0	+2.0	+5.0	+7.0
		$\%\Delta i$	0.3	1.4	2.7	3.3	3.8	3.6	3.0	2.3	1.7	1.0	0.6	−0.1	+0.3	+0.8	+1.0

TABLE III

Influence of frequency of X-rays on the Joshi effect in benzene vapour at different exciting potentials and constant intensity (anode current).

pC_6H_6 = 105 mm. at 27°. Frequency of A. C. supply = 50~. Source of X-radiations = Coolidge tube.

Exciting Potential in kV (r.m.s.).			2.0 mA						4.0 mA.					
			Frequency (anode-voltage)inkilovolts.											
			10.8	13.9	17.0	20.1	23.2	26.3	10.8	13.9	17.0	20.1	23.2	26.3
8.0	Current in dark i_D. 150	i_L	125	116	112	109	105	100	136	127	119	115	112	108
		$-\Delta i$	25	34	38	41	45	50	14	23	31	35	38	42
		$-\%\Delta i$	16.6	22.6	25.3	27.3	30.0	33.3	9.3	15.3	20.6	23.3	25.3	28.0
10.0	230	i_L	204	193	186	182	176	173	218	207	195	190	185	177
		$-\Delta i$	26	37	44	48	54	57	12	23	34	40	45	53
		$-\%\Delta i$	11.3	16.0	19.0	20.8	23.5	24.3	5.2	10.0	14.8	17.4	19.6	23.2
12.0	320	i_L	301	283	273	266	258	254	310	298	285	277	270	261
		$-\Delta i$	19	37	47	54	62	66	10	22	35	43	50	59
		$-\%\Delta i$	5.1	11.5	14.7	16.9	19.3	21.2	3.1	6.8	10.9	13.4	15.6	18.2
14.0	400	i_L	381	366	351	343	339	336	390	378	366	361	352	344
		$-\Delta i$	19	34	49	57	61	64	10	22	34	39	48	56
		$-\%\Delta i$	4.8	8.5	12.3	14.2	15.2	16.0	2.5	5.4	8.5	9.8	12.0	14.0
16.0	450	i_L	432	417	405	496	389	386	444	431	418	404	398	390
		$-\Delta i$	18	33	45	54	61	64	6	19	32	46	52	60
		$-\%\Delta i$	4.0	7.3	10.0	12.0	13.6	14.2	1.3	4.2	7.1	10.2	11.5	13.3
18.0	530	i_L	509	494	479	471	464	460	521	509	492	483	476	467
		$-\Delta i$	21	36	51	59	66	70	9	21	38	47	54	63
		$-\%\Delta i$	4.0	6.7	9.6	11.1	12.4	13.2	1.7	4.0	7.2	8.8	10.1	11.9

Nature, 1943, **151**, 561; Deo, *Indian J. Phys.*, 1944, **18**, 84; *Curr. Sci.*, 1944, **13**, 44; Mohanty and Kamath, this *Journal*, 1948, **25**, 467; Prasad, *Nature*, 1949, **164**, 69). The $-\%\triangle i$ in the visible increases initially almost linearly with light intensity and shows subsequently a tendency to saturation. Using various frequency bands in the visible, earlier workers have shown that $-\%\triangle i$ increases almost linearly with the mean frequency, despite an appreciable range of frequency variation (Deo, *loc. cit.* Tawde and Gopalkrishnan, *Proc. Ind. Acad. Sci.*, 1949, **29A**, 171; Mohanty, *loc. cit.* Deshmukh, *Proc. Nat. Inst. Sci.*, 1948, **25**, 197).

As can be seen from Table III and Fig. 2, unlike this linear increase of $-\%\triangle i$ with frequency in the visible region, $-\%\triangle i$ at first increases rapidly with the hardness of X-radiation but later on the increase becomes slow. Thus, at a constant intensity (4 mA) the $-\%\triangle i$ increases numerically from 9.3 to 20.6 as the frequency of X-rays varies from 10.8 to 17.0 kilovolts; while for equal increment *i.e.* from 17.0 to 23.2 kilovolts, increase is, however, small viz. from 20.6 to 25.3, exciting potential being 8.0 kV. For the same frequency variation and exciting potential the corresponding values of $-\%\triangle i$ for 2.0 mA are 16.6 to 25.3 and from 25.3 to 30.0 respectively. The curves in Fig. 2 indicate clearly the variation of $-\%\triangle i$ with frequency at different exciting potentials.

The absorption of X-rays by the glass wall (1 mm.) of the ozoniser was considered. Series of experiments were made in which the $\%\Delta i$ values were recorded for various intensities at fixed exciting potentials without and with the glass screen (4 mm. thick) interposed between the Coolidge tube and the ozoniser. Results show that the $\%\Delta i - I$ curve with the glass screen is closely similar to that when no glass screen is used on (Fig. 1). The curve with the glass screen on, however, is just a little lower than the other curve due to the small X-ray absorption by glass. Similar duplicates show that the $\%\triangle i - \nu$ (hardness) with the glass screen also lies slightly lower than, but resembles essentially that without the screen (Fig. 2). No sensibly disturbing factor is therefore introduced in the discussion due to glass wall absorption.

Joshi has shown (*Proc. Indian Sci. Cong.*, 1943, Part II, 70; *B. H. U. Jour.*, 1943, **8**, 99) on the basis of non-linearity of the $\%\triangle i - I$ relationship, that this phenomenon cannot be identified with a possible negative photoelectric effect. The results of Mohanty for oxygen (*loc. cit.*) and that of Prasad for mercury (*loc. cit*) confirm Joshi's view. These results in the visible are fairly well explained by Joshi's theory (*Curr. Sci.*, 1947, **16**, 19) according to which photoelectric emission from an electrode layer consisting of ions and excited particles, characterised by a low work function, is a primary seat of $\triangle i$; the released photoelectrons are captured by gas particles in the discharge space to form slow moving negative ions which reduce the current i as a space charge effect.

That the $\triangle i$ occurs under red region of the spectrum, which cannot photoionise the gas, as also under X-rays which should do so, shows that photoionisation in the gas phase is not fundamental to the production of $-\triangle i$. That the $\triangle i$ occurs appreciably both within and well outside the region of selective absorption suggests (Joshi, *Curr. Sci.*, 1945, **14**, 175; Vishvanathan, *Proc. Ind. Acad. Sci.*, 1948, **21A**, 300) that it is not a mere resonance effect; but some other type of quantal effect.

FIG. 1

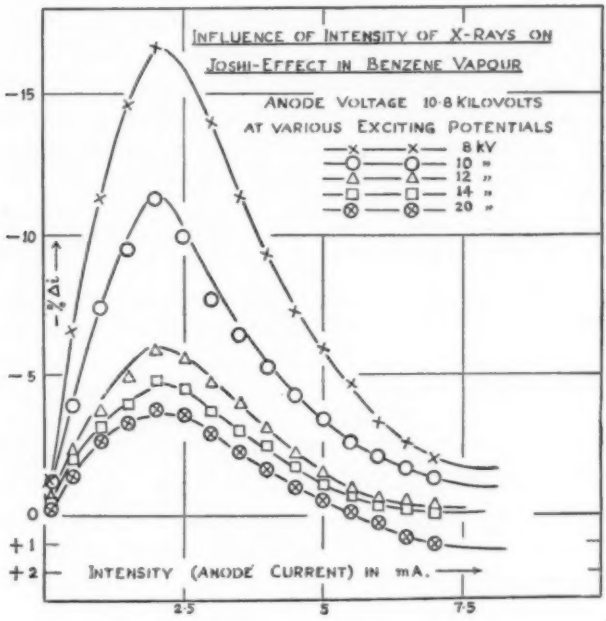
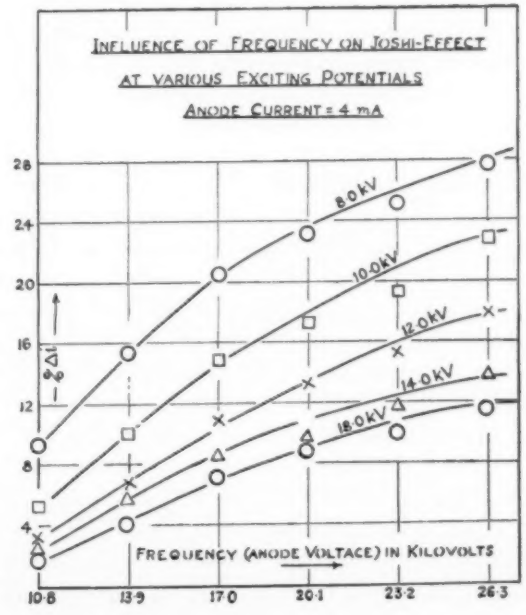

INFLUENCE OF INTENSITY OF X-RAYS ON
JOSHI-EFFECT IN BENZENE VAPOUR
ANODE VOLTAGE 10·8 KILOVOLTS
AT VARIOUS EXCITING POTENTIALS
8 kV
10 "
12 "
14 "
20 "
−15
−10
−5
0
+1
+2
−% Δi
INTENSITY (ANODE CURRENT) IN mA.
2·5
5
7·5

FIG. 2


INFLUENCE OF FREQUENCY ON JOSHI-EFFECT
AT VARIOUS EXCITING POTENTIALS
ANODE CURRENT = 4 mA
28
24
20
16
12
8
4
+ Δi
8·0 KV
10·0 KV
12·0 KV
14·0 KV
18·0 KV
FREQUENCY (ANODE VOLTAGE) IN KILOVOLTS
10·8
13·9
17·0
20·1
23·2
26·3

The results now reported, viz., the $-\%\triangle i$ increases (numerically) rapidly to a maximum, then decreases slowly and eventually changes sign, at large intensities of X-rays, can be explained on the behaviour of the space charge due to the positive ions in an ozoniser discharge (Part I, *loc. cit.*). It was shown therein on the essential analogy between an ozoniser discharge and the corona (the coaxial cylinder) that the discharge in the self-maintained region consisted of a number of high frequency current pulses due to the almost instantaneous electronic movement to the anode inter-spaced with 't_m', the time which is necessary for the traversal of the positive ions to the cathode (called the traversal time). This origin of the current pulses in the ozoniser discharge at and above the threshold potential V_m is similar to the Trichel pulses (*Phys. Rev.*, 1938, **54**, 1078; 1939, **55**, 382) observed in the corona. The application of the relation due to Montgomerys $i=Q/t_m$ and the suggested co-occurrence of $\pm \Delta i$ in benzene vapour (Part I, *loc. cit.*) are now discussed in the light of the mechanism of a counter.

On a careful examination of the current structure on the cathode ray oscillograph (208B Dumont) one finds that these current pulses can be grouped into two types (i) those having large and equal amplitude separated by approximately equal time intervals (ii) and those having relatively small and unequal amplitude appearing mostly between two consecutive pulses of class (i). These small puises may be called satellite pulses and appear similar to the 'multiples' or 'spurious pulses' occurring in a counter (Wilkinson, "Ionisation Chambers and Counters", Cambridge Univ. Press, 1950, p. 225).

When the positive ionic space charge, left behind by the initial avalanches after choking the discharge, crosses the region of intense ionisation, limited by the critical radius r_c, the field near the inner electrode (anode) is partially restored. A stray electron, produced between the r_c and the anode, ionises cumulatively starting a fresh avalanche of its own, before the initial positive ionic space charge has been cleared. This gives rise to satellite pulse which is not of a full amplitude, on account of the presence of positive ionic space charge in the gap restoring the field partially. These satellites continue to occur until the initial ionic space charge is cleared off the discharge space. The initial positive ionic sheath reaching the cathode gives rise to cathodic electrons starting the normal fuli amplitude pulses. The satellites are favoured in an ozoniser discharge which has an extended r_c. The amplitude of the current pulses is due to the change in the potential of the inner electrode caused by the collected charge (Ramsay, *Phys. Rev.*, 1940, **57**, 1022 ; Montgomeries, *ibid.*, p. 1030). The essential argument is not affected materially by considering the reversed polarity.

The simplified relation $i=Q/t_m$ (where Q is the charge collected by the anode and t_m =relaxation time) should include a factor 't_a', the active time, in denominator, during which mainly the electrons are collected. Because of the difference in mobilities of the electrons and ions, 't_m' is about a thousand time greater than 't_a' (which is ot the order 10^{-5} sec.). Thus 't_a' can be neglected in comparision to 't_m' in a simple approximation for the study of a counter. In a complex current structure of an ozoniser the inclusion of this factor and the corresponding effect of irradiation during 't_a' and 't_m' becomes important for the understanding of Δi phenomenon.

The effect of irradiation may now be considered in two stages :

(1) *During the active time.* Its significanc has been discussed in the earlier paper (this *issue*, p. 239).

(2) *Irradiation during 't_m'.* During this time, initial space charge (A) after crossing the critical radius r_c, increases the field near the cathode. Irradiation during this time increases t_m due to enhanced positive space charge which favours the production of satellite pulses. This is supported by the observation of Fenton and Fuller (*Proc. Phys. Soc.*, 1949, **62**, 32) that the probability for the occurrence of spurious pulses is accurately proportional to the charge generated in the discharge. This entails simultaneous occurrence of $+\Delta i$ during 't_m', due to increase in number (cf. Jatar, *J. Sci. Ind. Res.*, 1950, **9B**, 283) of satellites, and $-\Delta i$ as a result of the increase of 't_m'.

Effect of X-ray Intensity and Frequency.—On the above view as the intensity of the X-ray irradiation is increased, more photoelectrons are ejected from the cathode leading to a greater decrease in α during 't_a', and resulting in larger $-\Delta i$. At a critical intensity, it may be expected that due to the additional positive ionic space charge α cannot decrease further, hence, the peak obtained in $-\%\Delta i$ with intensity variation. A further increase in intensity causing increase in the number of photoelectrons will presumably favour the production of sattellites leading to an increase in the $+\Delta i$ component of the resultant effect.

As the frequency is encreased, the photoelectrons emitted from the cathode will possess higher energy and consequently a greater reduction in α, as envisaged during 't_a' leading to larger $-\Delta i$.

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HETEROPOLY ACIDS OF NIOBIUM AND TANTALUM WITH IODIC AND PERIODIC ACIDS

By Debabrata Sen and Priyadaranjan Rây

The preparation and properties of some heteropoly acids of niobium and tantalum with iodic and periodic acids have been described. Their composition can be represented by the general formula, $R_2O_5.1$ or $2\ HIO_3(HIO_4).\ xH_2O$; where R = Nb or Ta.

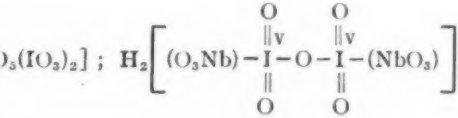
Niobium and tantalum have been found to give various complexes with oxalic acid (Russ, *Z. anorg. Chem.*, 1902, **31**, 42) and tartaric acid (Srinivasan, *Proc. Ind. Acad. Sci.*, 1950, **31A**, 194). Formation of complexes with catechol, pyrogallol, salicylic acid, salicylaldehyde, acetylacetone (Rosenheim and Roehrich, *Z. anorg. Chem.*, 1932, **204**, 342); 8-hydroxyquinoline (Süe, *Compt. rend.*, 1933, **196**, 1022); phenol, β-naphthol etc. (Funk and Baumann, *Z. anorg. Chem.*, 1937, **231**, 264) has also been reported. Insoluble complex compounds of hypophosphorous acid with niobium and tantalum have been described by Alimarin and Burova (*J. Appl. Chem. USSR.*, 1945, **18**, 286). Uspenskya and Chernikov (*Compt. rend. Acad. Sci., USSR.*, 1940, **28**, 800) claim to have separated Nb and Ta by precipitating Ta from its oxalato complex by the addition of iodic acid. The exact composition of the complex has not, however, been given.

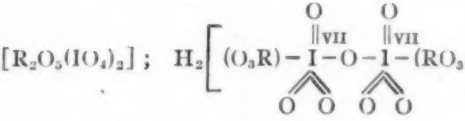
The neighbours of Nb and Ta in the IV group of the Periodic Table such as Ti, Zr and Th, all are known to give simple and double iodates. Similarly molybdenum and tungsten of the VI group also give rise to complex heteropoly acids with iodic acid. It is also well known that vanadium, the lower homologue of Nb and Ta, forms various heteropoly acids with iodic and periodic acids (Rosenheim and Yang, *Z. anorg. Chem.*, 1923, **129**, 181).

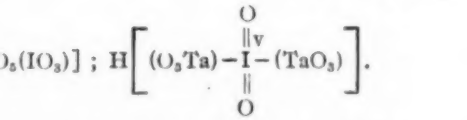
It was therefore considered interesting to examine whether Nb and Ta too formed heteropoly acid complexes of a similar type. With this end in view, an attempt was made to prepare the iodates and periodates of Nb and Ta following the method of Rây and Saha (*ibid.*, 1932, **208**, 100), employed for the preparation of titani-iodates. This has led to the preparation of the following compounds:

1. $Nb_2O_5.2HIO_3.2H_2O (Nb_2O_5.I_2O_5.3H_2O)$.
2. $Nb_2O_5.2HIO_4.8H_2O (Nb_2O_5.I_2O_7.9H_2O)$.
3. $Ta_2O_5.HIO_3.6H_2O (2Ta_2O_5.I_2O_5.13H_2O)$.
4. $Ta_2O_5.2HIO_4.2H_2O (Ta_2O_5.I_2O_7.3H_2O)$.

All these compounds lose most of their water molecules at about 110°—115° retaining only those necessary for their constitution as indicated above by the first mode of formulating their composition. They are therefore best represented as complex heteropoly acids of the structure:

1. $H_2[Nb_2O_5(IO_3)_2]$; 

2. & 4. $H_2[R_2O_5(IO_4)_2]$;  ; R=Nb or Ta.

3. $H[Ta_2O_5(IO_3)]$; 

On this basis, iodato-niobic acid (1) and periodato-niobic and tantalic acids (2 and 4) become binuclear heteropoly acids with an oxygen bridge, and iodato-tantalic acid forms mononuclear heteropoly acid, with quinquevalent and septivalent iodine as the central atom in the iodato- and periodato-acids respectively. The co-ordination number of iodine in these heteropoly acids is six with the oxygen atoms occupying one or two positions each. All the substances are acidic to litmus and liberate iodine from potassium iodide solution even without the addition of any acid, which indicates that they are really acids.

Alternatively, they may be regarded as derivatives of ortho-iodic and ortho-periodic acids as shown below :

1. $I(OH)_5 \longrightarrow I_2O(OH)_8 \longrightarrow I_2O_3(OH)_4 \longrightarrow \begin{bmatrix} I_2O_3 & (NbO_3)_2 \\ & (OH)_2 \end{bmatrix}$.

3. $I(OH)_5 \longrightarrow IO(OH)_3 \longrightarrow \begin{bmatrix} IO & (TaO_3)_2 \\ & OH \end{bmatrix}$.

2. & 4. $I(OH)_7 \longrightarrow I_2O(OH)_{12} \longrightarrow I_2O_5(OH)_4 \longrightarrow \begin{bmatrix} I_2O_5 & (OH)_2 \\ & (RO_3)_2 \end{bmatrix}$

[where R=Nb or Ta.]

EXPERIMENTAL

Iodato-niobic Acid.—Iodic acid was dissolved in nitric acid (1 : 1) and addedd dropwise to a filtered solution of potassium niobifluoride in 50% nitric acid with constant stirring. This was taken in a platinum basin and was warmed on the water-bath. A white milky precipitate was formed, which was thoroughly stirred with a platinum spatula. The mixture was warmed on the bath till all the hydrofluoric acid was removed. A white crystalline precipitate settled down ; this was cooled and washed four to five times with nitric acid (1 : 1) by decantation to free it from any fluoride ion. The product was then filtered through a sintered glass funnel and washed thoroughly with 50% nitric acid solution. The substance was dried in a desiccator over sulphuric acid and potassium hydroxide.

The substance forms a white powder, insoluble in water and also in organic solvents. On heating, it gives off violet vapours of iodine. A suspension of the substance in water liberates iodine from potassium iodide solution. It is acidic to litums.

Niobium was estimated by igniting the compound in a platinum crucible and weighing as Nb_2O_5. The iodate was estimated by treating the substance with a solution of potassium iodide and acetic acid, and titrating the liberated iodine with standard thiosulphate solution. [Found : Nb, 28.37 ; IO_3, 53.24 ; H_2O (by loss at 110°−115°), 5.49. $Nb_2O_5.2HIO_3.2H_2O$ requires Nb, 28.40 ; IO_3, 53.51 ; H_2O, 5.50 per cent]. [Found (dried at 110°−115°.) : Nb, 30.02 ; IO_3, 56.60. $Nb_2O_5.2HIO_3$ requires Nb, 30.05 ; IO_3, 56.63 per cent].

Periodato-niobic acid was prepared from a solution of potassium periodate in 50% nitric acid and that of potassium niobifluoride in the same acid following the method described above. The substance resembles the iodato-niobic acid in all its properties.

Periodate ion was estimated by titrating with standard thiosulphate, the iodine liberated by the substance from acidified potassium iodide. [Found : Nb, 23.37 ; IO_4, 48.15; H_2O (by loss at 110°−115°), 18.18. $Nb_2O_5.2HIO_4.8H_2O$ requires Nb, 23.40 ; IO_4, 48.10 ; H_2O, 18.13 per cent].

[Found (dried at 110−115°) : Nb, 28.63 ; IO_4, 58.79. $Nb_2O_5.2HIO_4$ requires Nb, 28.60 ; IO_4, 58.77 per cent].

Iodato-tantalic acid was prepared exactly like the the corresponding niobium compound using potassium tantalifluoride in place of potassium niobifluoride.

The substance forms a white powder, and resembles the corresponding niobium compound in properties. [Found : Ta, 49.87; IO_3, 24.12; H_2O (by loss at 110°−115°), 14.89. $Ta_2O_5.HIO_3.6H_2O$ requires Ta, 49.86 ; IO_3, 24.10 ; H_2O, 14.87 per cent].

[Found (dried at 110°−115°) : Ta, 58.59 ; IO_3, 28.33. $Ta_2O_5.HIO_3$ requires Ta, 58.57 ; IO_3, 28.32 per cent].

Periodato-tantalic acid was prepared exactly like the corresponding niobium compound using potassium tantalifluoride in place of potassium niobifluoride. It resembles its niobium analogue in properties. [Found : Ta, 41.95 ; IO_4, 44.33 ; H_2O (by loss at 110°−115°), 4.15. $Ta_2O_5.2HIO_4.2H_2O$ requires Ta, 41.99 ; IO_4, 44.31 ; H_2O, 4.19 per cent].

[Found (dried at 110°−115°) : Ta, 43.81 ; IO_4, 46.26. $Ta_2O_5.2HIO_4$ requires Ta, 43.82 ; IO_4, 46.24 per cent].

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STUDIES ON THE CHEMISTRY OF RHENIUM. PART III. COMPLEX COMPOUNDS OF QUADRIVALENT RHENIUM WITH CATECHOL

By Debabrata Sen and Priyadaranjan Rây

A complex acid formed by quadrivalent rhenium with catechol, having the composition, $H[(OH)_3.Re.C_6H_4O_2.H_2O]$, and its thallium salt have been described. The dissociation constant, k, of the acid has also been determined, which gives a value of 3.2×10^{-5} at 25°.

In continuation of the work described in Parts I and II of this series (this *Journal*, 1953, **30**, 171, 181), a complex acid of quadrivalent rhenium with catechol and its thallium salt are now described in the present paper.

The precipitated rhenium dioxide ordinarily does not dissolve in a solution of catechol even when boiled. But on heating potassium rhenichloride with catechol in water, a dark brown solution was obtained from which brown crystals of a complex compound were isolated. It was found on analysis to have the composition $ReO\ C_6H_4O_2.3H_2O$. The three molecules of water could not be removed without decomposition. The structure of the complex can therefore be represented as: $H[Re.(OH)_3.C_6H_4O_2.H_2O]$ or, $H_2[Re.(OH)_4.C_6H_4O_2]$. Potentiometric titration with alkali showed the acid to have a monobasic character. The substance should therefore be represented by the first formula.

The value of k, the dissociation constant, has been found to be 3.2×10^{-5} at 25°. The dissociation constant of catechol is 3.3×10^{-10} at 25° (Euler and Bölin, *Z. physikal. Chem*, 1909, **66**, 75). Thus, the complex formation has considerably increased the strength of the acid. The thallium salt of this acid has also been prepared.

Experimental

Aquo-trihydroxo-rheni-catechol.—Pure recrystallised potassium rhenichloride (1 mol.) was treated with catechol (4 mols., Merck's Reagent) in a little water. The mixture was then heated just to boiling in a R. B. flask under reflux and then warmed on the water-bath for about an hour. A dark brown solution was obtained which was cooled, filtered and evaporated to dryness in a vacuum desiccator over concentrated sulphuric acid. The residue was extracted with absolute alcohol to remove potassium chloride. The alcoholic solution was again evaporated to dryness in a vacuum desiccator. The product was then digested with dry and pure ether to remove the excess of catechol. The residue of the complex acid was washed thoroughly with ether and kept in a desiccator over concentrated sulphuric acid.

The substance forms brownish black crystals, which reacts acid in aqueous solution. It is highly soluble in water and alcohol and also in dioxane, but insoluble in dry ether. It is quite stable in acid medium, but slowly oxidises in presence of alkali.

Rhenium was estimated as in the case of rhenigallic acid described before. Carbon and hydrogen were estimated by combustion in a semimicro combustion system.

{Found : Re, 51.06 ; C, 19.79 ; H, 2.69. $H[Re.(OH)_3.C_6H_4O_2.H_2O]$ requires Re, 51.10 ; C, 19.78 ; H, 2.75 per cent}.

Potentiometric Titration of the Acid.—The acid was titrated against alkali potentiometrically (cf. Figs. 1-2) (cf. Part II, *loc. cit.*).

Fig. 1

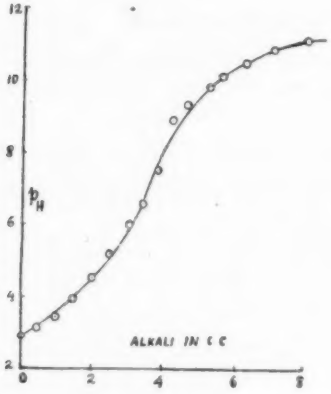

Fig. 2

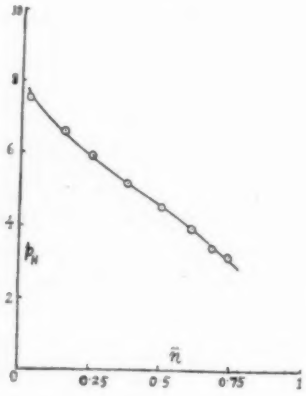

TABLE I

Alkali = 0.1247 *M*. t = 25°. Acid = 0.005 *M*.

Alkali.	Molar conc	p_H.	pk.	n.
0.0 c.c.	—	3.00	3.602	0.800
0.5	0.6253×10^{3}	3.15	3.591	0.734
1.0	1.247	3.42	3.737	0.675
1.5	1.871	3.95	4.152	0.603
2.0	2.494	4.52	4.512	0.495
2.5	3.118	5.20	4.978	0.375
3.0	3.742	6.00	5.526	0.252
3.4	4.240	6.62	5.873	0.152
3.8	4.740	7.54	6.279	0.052
4.2	—	8.93	—	—
5.0	—	9.82	—	—

From Fig. 2, $pk = 4.5$; $k = 3.2 \times 10^{-5}$.

Thallium salt of the aquo-trihydroxo-rheni-catechol was prepared by the addition of thallous sulphate to a solution of rheni-catechol in water. The insoluble thallous salt separated out as a brown precipitate. This was filtered, washed thoroughly with water and then with a little alcohol. It was finally dried in a desiccator over concentrated sulphuric acid.

The substance forms dark brown crystals, almost insoluble in water and organic solvents, but soluble in dilute mineral acids.

The substance was analysed following the method employed for the thallium salt of rhenigallic acid described in the previous paper (*loc. cit.*). {Found:Re, 32.84; Tl, 35.87. Tl $[Re.(OH)_3.C_6H_4O_2.H_2O]$ requires Re, 32.80 ; Tl, 35.98 per cent}.

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STUDIES ON THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART V. CADMIUM ACETATE

By S. Aditya and B. Prasad

The nature of cadmium acetate has has been studied from the E. M. F. measurements of the cells--

(A) $Cd_xHg_y \mid Cd(NO_3)_2 \parallel$ bridge $\parallel Cd\,Ac_2(c)\ HAc(c_1) \mid Cd_xHg_y$

(B) $Hg, Hg_2Ac_2 \mid CdAc_2(c)\ HAc(c_1) \parallel$ bridge $\parallel NaAc(ac)\ HAc(c_1) \mid Hg_2Ac_2, Hg$

and (C) $Hg, Hg_2Ac_2 \mid CdAc_2(c)\ HAc(c_1) \mid Cd_xHg_y$.

The constants for the first stage of dissociation, $CdAc \rightleftarrows CdAc^+ + Ac^-$ is 1.0×10^{-1} and that of the second stage, $CdAc^+ \rightleftarrows Cd^{++} + Ac^-$ is 1.7×10^{-2}. These have been calculated from the study of the cells 'A' and 'B' on some assumptions. The study of the cell 'C' justifies these assumptions.

Cadmium has a great tendency to co-ordination and its salts very often form auto-complexes in solution. The variation of transport number with concentration is ascribed to the formation of complexes. The behaviour of its chlorides and bromides has been studied by Riley and Gellafant (*J. Chem. Soc.*, 1932, 514).

Farrel, Ridgeon and Riley (*ibid.*, 1934, 1440) studied the reaction between cadmium ion and different carboxylic acid by means of potentiometric titration. They conclude that mostly undissociated cadmium acetate is formed. Their values of K_1 corresponding to $CdAc_2 \rightleftharpoons CdAc^+ + Ac^-$ vary from 0.63×10^{-2} to 2×10^{-2}. They did not take interionic forces into account.

Quintin (*Compt. rend.*, 1941, **212**, 855) measured the conductance of cadmium acetate and concluded that cadmium acetate was only partially dissociated. Subsequently, however, he (*J. chim. phys.*, 1942, **77**, 39) ascribed the deviation rather to hydrolysis than to the association of ions.

Leden (*Svensk Kem. Tid.*, 1946, **58**, 129) has reported the existence of $CdAc^+$ and $CdAc_4^{--}$ ions.

In the present work the study of the following cells was undertaken to throw light on the nature of cadmium acetate in solution.

$$Cd_xHg_y \mid Cd(NO_3)_2\ (c) \parallel \underset{\text{bridge}}{\text{Salt}} \parallel CdAc_2(c)\ HAc(c_1) \mid Cd_xHg_y \quad \ldots\ (1)$$

$$Hg \mid Hg_2Ac_2 \mid CdAc_2(c)\ HAc(c_1) \parallel \underset{\text{bridge}}{\text{Salt}} \parallel NaAc(c)\ HAc(c_1)\ Hg_2Ac_2 \mid Hg \quad \ldots\ (2)$$

$$Hg, Hg_2Ac_2 \mid CdAc_2(c) HAc(c_1) \mid Cd_xHg_y \quad \ldots \quad \ldots\ (3)$$

The junction potential is practically eliminated as pointed out in previous communications (this *Journal*, 1952, **29**, 169 ; 1953, **30**, 213, 217).

EXPERIMENTAL

The E.M.F. of all the cells were studied in an air thermostat kept at 30°. In all the cases cadmium amalgam of the same composition, prepared as described in Part IV of this series (this *Journal*, 1953, **30**, 217) was used. Cadmium acetate trihydrate and cadmium nitrate (both Merck and Co., A.R.) were used. The cadmium acetate trihydrate was found to be 100% pure as tested volumetrically by oxine method. All solutions of cadmium acetate were made by direct weighing. Cadmium nitrate being hygroscopic, a stock solution was made and its concentration was estimated as above. All necessary solutions were made from this. The cell vessels and the bridge used were of the type described earlier (this *Journal*, 1951, **28**, 683). Each half cell of the cells I and II was prepared in duplicate. The duplicate cells were joined to each other by means of a rubber tubing containing the same solution as in the duplicate cells and the E.M.F. was measured, and if it exceeded 0.1 m.v., the half cells were discarded. Then the cells of the type I and II were set up by joining the proper half cell by means of salt bridge. The E.M.F. of these cells did not differ by more than 0.2 m.v. In every case the mean of the two was taken. The cell III was always set up in duplicate and the E.M.F. agreed within 0.1 m.v.

The E.M.F. of the cell

$$Cd_xHg_y \mid \underset{(c)}{Cd(NO_3)_2} \parallel \underset{NH_4NO_3\ \text{bridge}}{\text{Saturated}} \parallel CdAc_2(c)HAc\ (c_1) \mid Cd_xHg_y$$

having the same molar concentration of cadmium nitrate and cadmium acetate but different concentration of acetic acid gave a linear plot against the concentration of acetic acid, and the values of E.M.F. corresponding to zero concentration of acetic acid as found by extrapolation are given in column 4 of Table I.

If activity coefficients are assumed to be unity and cadmium acetate dissociates as

$$\underset{c}{2CdAc_2} \rightarrow \underset{c/2}{Cd^{++}} + \underset{{}_4(1-\gamma)c/2}{CdAc^{--}}$$

$$\uparrow\downarrow$$

$$\underset{\gamma c/2}{Cd^{++}} + \underset{2\gamma c}{4Ac^-}$$

the E.M.F. of the concentration cell $Cd_xHg_y \mid Cd(NO_3)_2 \parallel$ bridge $\parallel CdAc_2,\ HAc \mid Cd_xHg_y$ will be given by

$$E = \frac{RT}{2F} \log \frac{2}{1+\gamma},$$

as cadmium nitrate is completely dissociated (Part IV, *loc. cit.*). When the dissociation is calculated with this equation, the value γ becomes negative in four out of six cases (negative in concentration 0.04, 0.06, 0.08, 0.1*M*). Hence, this scheme is discarded.

If cadmium acetate dissociates in the following way,

$$CdAc_2 \underset{(1-\alpha)\beta c}{\overset{\leftarrow}{\rightarrow}} CdAc^+ + \underset{\beta c}{Ac^-}$$

$$\downarrow\uparrow$$

$$\underset{\alpha\beta c}{Cd^{++}} + \underset{\alpha\beta c}{Ac^-}$$

the E.M.F. of the above cell will be given by the equation

$$E_1 = \frac{RT}{2F} \log \frac{a_{Cd^{++}} \text{ in } Cd(NO_3)_2 \text{ solution}}{c\alpha\beta f_{Cd^{++}} \text{ in } CdAc_2 \text{ solution}}.$$

The activity coefficient of cadmium nitrate is not found in literature. As cadmium nitrate is completely dissociated, the activity coefficient of cadmium ion ($a_{Cd^{++}}$) in cadmium nitrate may be assumed to be equal to that of barium chloride of the same ionic strength and calculated on the lines given by Lewis ("Thermodynamics", 1923, p. 379). Knowing E_1 and $a_{Cd^{++}}$ it was possible to calculate $\alpha\beta f_{Cd^{++}}$.

On the basis of the same scheme of dissociation, the E.M.F. of the cell

$$\underset{(c)}{Hg} \mid \underset{(c_1)}{Hg_2Ac_2CdAc\ HAc} \parallel \underset{NH_4NO_3 \text{ bridge}}{\text{Saturated}} \parallel \underset{(2c)}{NaAc\ HAc} \underset{(c_1)}{Hg_2Ac_2} \mid Hg,$$

extrapolated to zero concentration of acetic acid is given by

$$E_2 = \frac{RT}{F} \log \frac{a_{Ac^-} \text{ in NaAc solution}}{c\beta(1+\alpha) f_{Ac^-} \text{ in } CdAc_2 \text{ solution}}.$$

The E.M.F. values of these cells are given in Table II.

The activity of acetate ion was assumed in sodium acetate to be equal to that of chloride ion in sodium chloride at the same ionic strength since both sodium chloride and sodium acetate solutions were dilute and completely dissociated and of the same valence type. So it became possible to calculate the value of a_{Ac^-} in sodium acetate solution and that of $\beta(1+\alpha)f_{Ac^-}$ in cadmium acetate solution.

The ionic strength (μ) of the cadmium acetate solutions is given by $\mu = \beta c(1+2\alpha)$. Assuming $f_{Cd^{++}}$ and f_{Ac^-} to be unity, a rough value of α, β and ionic strength is obtained from the values of $\alpha\beta f_{Cd^{++}}$ and $\beta(1+\alpha)f_{Ac^-}$ known earlier. From this rough value of ionic strength it is possible to find out a value of $f_{Cd^{++}}$ and f_{Ac^-} in cadmium acetate on the basis: (1) the activity coefficient of cadmium ion in cadmium acetate solution is equal to that of barium ion in barium chloride solution of the same ionic strength and (2) the activity coefficient of acetate ion is equal to that of chloride ion in the solution of the same ionic strength. The values of α, β, μ as well as $f_{Cd^{++}}$ and f_{Ac^-} are then correctly determined by the method of approximations. About three approximations are enough. The final value of α and β are given in columns 5 and 6 of Table II.

The values of K_1 and K_2 are given by the following equations,

$$K_1 = \frac{a_{CdAc^+} \times a_{Ac^-}}{a_{CdAc_2}} = \frac{(1-\alpha)\beta c(1+\alpha)\beta c f_{CdAc^+} f_{Ac^-}}{(1-\beta)c f_{CdAc_2}} = \frac{(1-\alpha^2)\beta^2 c\, f_{CdAc^+} f_{Ac^-}}{(1-\beta)}.$$

TABLE I

Cell : Cd_xHg_y | $Cd(NO_3)_2$(c) || Salt bridge || $CdAc_2$(c)HAc(c_1) | Cd_xHg_y.

Concentration of cadmium acetate and cadmium nitrate.	Concentration of acetic acid.	E M F.(mean of of the duplicate).	Extrapolated value of E.M.F.
0.01 *M*	0.005 *M*	0.0063	0.0064
	0.010	0.0060	
	0.015	0.0055	
	0.020	0.0054	
0.02	0.005	0.0077	0 0075
	0.010	0.0069	
	0.015	0 0068	
	0.020	0 0067	
0.04	0.005	0.0106	0.0107
	0.010	0.0104	
	0.015	0.0103	
	0.020	0.0103	
0.06	0.005	0.0114	0.0116
	0 010	0.0113	
	0.015	0.0111	
	0.020	0.01085	
0.08	0.005	0.0137	0.0142
	0.010	0.0126	
	0.015	0.0120	
	0.020	0.0115	
0.1	0.005	0.0159	0.0164
	0.010	0.0153	
	0.015	0.0148	
	0.020	0.0144	

In arriving at the last term the activity coefficient of undissociated cadmium acetate is taken to be unity. Further, the activities of monovalent $CdAc^+$ and Ac^- ions are taken to be equal to that ot the chloride ion in solutions having the same ionic strength. The values of K_1, thus determined, are given in column 7 of Table II and the mean value is 1×10^{-1}.

$$K_2 = \frac{a_{Cd^{++}} a_{Ac^-}}{a_{CdAc^+}} = \frac{\beta(1+\alpha)c f_{Ac^-} \alpha \beta c f_{Cd^{++}}}{\beta(1-\alpha)c\, f_{CdAc^-}} = \frac{(1+\alpha)\beta c \alpha f_{Cd^{++}}}{(1-\alpha)}$$

TABLE II

Cell : Hg, Hg_2Ac_2 | $CdAc_2$(c) HAc(c_1) || Salt || NaAc(2c)HAc(c_1) | Hg_2Ac_2,Hg.
bridge

Conc. of $CdAc_2$.	Conc. of acetic acid.	E.M.F.	Extrapolated E.M.F.	β.	α.	K_1.	K_2.
0.01 *M*	0.005 *M*	0.0054	0.0054	1.00	0.6073	...	1.406×10^{-2}
	0.010	0 0054					
	0.015	0.0055					
	0.020	0.0055					
0.02	0.005	0.0090	0 0090	0.915	0.5508	0.977×10^{-1}	1.717×10^{-2}
	0.010	0.0089					
	0.015	0.0091					
	0.020	0.0091					
0.04	0.005	0.0127	0 0126	0.855	0.4421	0.816×10^{-1}	1.667×10^{-2}
	0.010	0.0126					
	0.015	0.0128					
	0.020	0.0128					
0.06	0.005	0.0148	0.0148	0.785	0.4420	0.822×10^{-1}	2.04×10^{-2}
	0.010	0.0146					
	0.015	0.0148					
	0.020	0.0148					
0.08	0.005	0.0156	0.155	0.8001	0.3473	1.300×10^{-1}	1.646×10^{-2}
	0.010	0.0155					
	0.015	0.0157					
	0.020	0.0157					
0 1	0.005	0.0181	0.0180	0.7381	0.3121	1.048×10^{-1}	1.410×10^{-2}
	0.010	0.0181					
	0.015	0.0182					
	0.020	0.0183					

Mean value of $K_1 = 1.0\times10^{-1}$.
Mean value of $K_2 = 1.7\times10^{-2}$.

The values of K_2 are given in column 8 of Table II and the mean is 1.7×10^{-2}.

For the cells of $HgHg_2Ac_2$ | $CdAc_2$(c)HAc(c_1) | Cd_xHg_y the electrode vessels were the same as used in the study of $HgHg_2Ac_2$ | $PbAc_2$ | Pb_xHg_y (Part III, *loc. c.t.*). Here also, acetic acid was added to suppress hydrolysis. The experimental data are given in Table III. The column 4 gives the extrapolated values. The E.M.F. of this type of cell extrapolated to zero concentration of acetic acid is given by

$$E_3 = E_0 - \frac{RT}{2F}\log \alpha\beta c f_{cd^{++}}(1+\alpha)^2\beta^2c^2f^2_{\pm\bar{c}}.$$

TABLE III

Cell : $Hg\ Hg_2Ac_2 \mid CdAc_2(c)HAc(c_1) \mid Cd_xHg_y$.

Conc of CdAc.	Conc. of acetic acid.	E.M.F. observed.	Extrapolated E.M.F.	E_0 calculated.
0.01 *M*	0.005 *M*	1.04315	1.0431	0.8574
	0.010	1.04310		
	0.015	1.04295		
	0.020	1.04310		
0.02	0.005	1.0253	1.0252	0.8582
	0.010	1.0255		
	0.015	1.0255		
	0.020	1.0255		
0 04	0.005	1.0078	1.0077	0.8576
	0.010	1.0079		
	0.015	1.0081		
	0.020	1.0082		
0.06	0.005	0.9981	0.9905	0.8581
	0.010	0.9984		
	0 015	0.9984		
	0.020	0.9982		
0.08	0.005	20.99055	0.9905	0.8569
	0.010	0.99065		
	0.015	0.9908		
	0.020	0.9916		
0.1	0.005	0.9875	0.9885	0.8568
	0.010	0.9873		
	0.015	0.9865		
	0.020	0.9860		

Mean value of E°=0.8575 volt.

The values of α and β, $f_{Cd^{++}}$ and f_{Ac^-} for the various concentrations of cadmium acetate are known from the study of the cells I and II. With the values of E_2, obtained as described above, it is possible to calculate the value of E_0 in case of each cell and the values are given in Table III. The values of E_0 do not differ from the mean by more than 0.7 m.v. This may be taken to be a justification for the assumptions regarding the elimination of liquid junction potential and the values of activity coefficients.

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CYANINE DYES FROM β-NAPHTHAQUINALDINE

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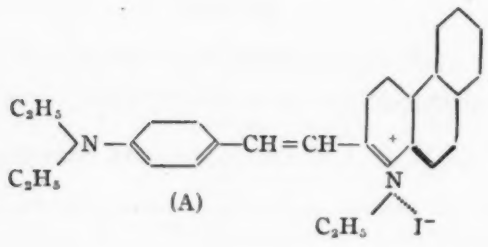
Four new cyanine dyes have been prepared by the condensation of β-naphthaquinaldine ethiodide with *p*-diethylaminobenzaldehyde, *p*-toluquinaldine ethiodide, 6-ethoxyquinaldine ethiodide and *p*-toluquinoline ethiodide, and their optical, photographic and other properties studied. The effect of the change of molecular weight, structure and substituents on the sensitising power of these and other related compounds has been discussed.

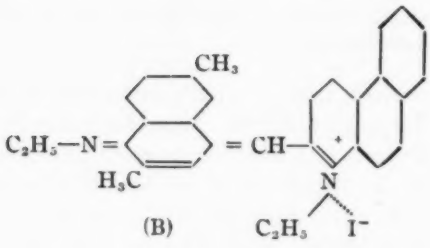
Cyanine dyes derived from β-naphthaquinaldine are known to be good sensitisers (Mills and Pope, *Phot. J.*, 1920, **60**, 193; Mees and Gutekunst, *Ind. Eng. Chem.*, 1922, **14**, 1060; Hamer, *J. Chem. Soc.*, 1928, 212; Hamar and Kelly, *ibid.*, 1931, 778; D. R. P. 158349). Recent work has shown (Leermarkers, Carrol and Stand, *J. Chem. Phys.*, 1937, **5**, 378; Schwarz, *Sci. Ind. Phot.*, 1939, **10**, 233; Levkoev and Natanson, *Acta Physicochem.*, 1946, **21**, 437; Brooker and Eastman Kodak Co., U. S. P. 2461137/1949; Dickinson, *Phot. J.*, 1950, **90B**, 142) that even minor structural changes, such as the replacement of one small group by another, considerably affects the aggregation of cyanine dyes, and consequently changes their sensitising power. Further impetus to the preparation of new types of dyes has been given by the observation that the sensitising efficiency of a cyanine dye is increased by an admixture with another dye, which may or may not possess a sensitising characteristic itself (Hamar, *Quart. Rev.*, 1950, **4**, 353). This is known as "supersensitisation". It is an important advance, and a number of compounds have been claimed as supersensitisers (B.P. 518478, 518067; U. S. P. 2398778, 2380940). This has been of great help in the preparation of highly sensitive, special quality photographic emulsions (Kendal, *Phot. J.*, 1950, **90B**, 165). In view of these considerations we have attempted to prepare a few new β-naphthaquinaldine-derived cyanine dyes.

Four compounds have been prepared and investigated. (A) has been obtained by the condensation of β-naphthaquinaldine ethiodide with *p*-diethylaminobenzaldehyde under the catalytic influence of piperidine. This belongs to the "Pinaflavol" type of cyanine dyestuff. (B), (C) and (D) have been obtained by the interaction of β-naphthaquinaldine ethiodide with *p*-toluquinaldine ethiodide, 6-ethoxyquinaldine ethiodide and *p*-toluquinoline ethiodide respectively, in the presence of alcoholic KOH. They are all cyanine dyes of the "*iso*cyanine" type and differ from one another only in the nature of the substituents in the 2′ and 6′ positions of the quinoline nucleus. Whereas (B) has methyl groups in both these positions, (C) has one methyl and one ethoxyl group, and (D), only one methyl group in the 6′ position.

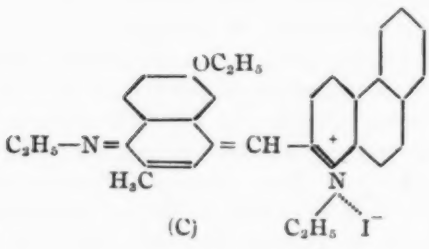
[Note—According to the modern concept of the the structure of cyanine dyes, the positive charge of the cation is distributed over the two basic groups, the molecule being regarded as a resonance hybrid of two canonical structures. The formulae shown below therefore represent resonance extremes only].



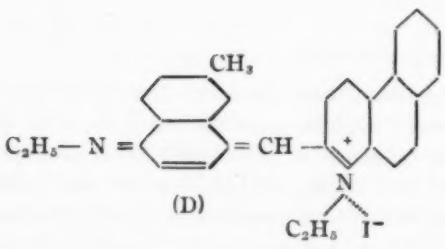
(A)



(B)



(C)



(D)

β-Naphthaquinaldine ethiodide has been used by several workers in the synthesis of cyanine dyes, but nowhere we have been able to find its preparation details. We obtained β-naphthaquinaldine by the method of Döbner and von Miller (*Ber.*, 1884, **17**, 1711), and the base was quaternised by a prolonged water-bath heating in a sealed tube with a slight excess of ethyl iodide.

In regard to yield (A) gives the highest (72.8%). Among the *iso*cyanines (D) is the best with a yield of 43.8%; (B) comes next with 28.28 and (C), last with 24.06%.

(A) being the lightest molecule it has the lowest melting point, 189°. Again of the three *iso*cyanines, (D) has the lowest molecular weight and therefore perhaps possesses the lowest m.p. 218°. This, however, is not the rule. (C), although heavier than (B), has a lower m.p., 220° and 225° respectively. All the four compounds are readily soluble in methyl and ethyl alcohol and insoluble in ether. (B) is only slightly soluble in chloroform, but (C), (D) and (A) dissolve a little more. (A) is soluble in water and becomes more so on warming. The other three compounds dissolve less easily in this solvent.

Alcoholic solutions of these compounds are all coloured with a red-violet shade. Their relative intensities are given in column 6 of Table I. These have been colorimetrically determined for 1 : 50,000 solutions in rectified spirit. It will be noticed that the pinaflavol compound (A) is the most intensely coloured and the diethyl *iso*cyanine (B), the least so.

Their solutions are decolorised by acids. It has been suggested that this process involves the addition of a proton to the methin chain and consequently the loss of resonance stabilisation, which is responsible for the colour (Maccoll, *Quart. Rev.*, 1947, **1**, 50; Brooker *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1889). The relative resistance to decolorisation of these dyestuffs is given in column 5 of Table I. It will be seen that (A) is pronouncedly much more resistant than the other three compounds. (C) and (D) are almost equally resistant.

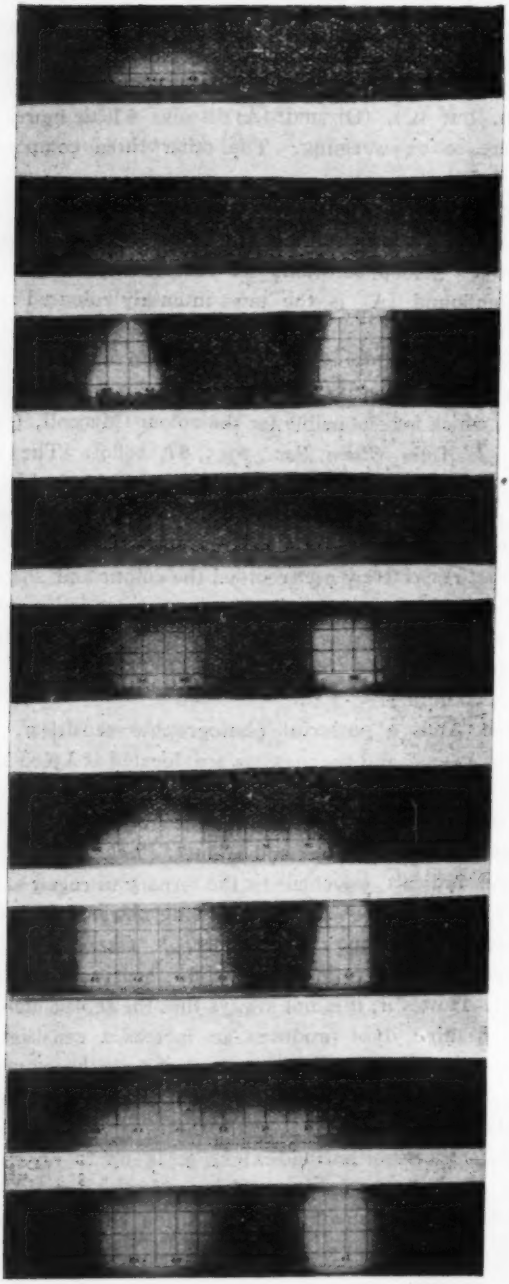
In columns 2,3 and 4 respectively are recorded the colour and shape of the crystals of these compounds, their reflexes and the pleochroic characteristics exhibited by them.

The sensitisation spectra of the new dyes are given in Fig. 1, along with that of an unbathed plate for the purpose of comparison. Their salient features have been summarised in Table I, column 7.

The first compound (A) is a powerful photographic sensitiser. The sensitisation has been extended to λ7400, and the maxima are located at λ5600 and λ6600. It is of interest to note in this connection that the corresponding dimethyl compound, that is to say the 2-*p*-dimethylaminostyryl-β-naphthaquincline ethiodide, sensitises only up to λ7000 with a maximum at λ6200 (Bloch and Hamer, *Phot. J.*, 1930, **70**, 386). Thus by changing the alkyl radicals attached to the ternary nitrogen atom, from methyl to ethyl, there has been an augmentation of the sensitising power, which is more than that produced by the addition of a benzene ring (Hamer, *J. Chem. Soc.*, 1930, 999). 2-*p*-Dimethylaminostyryl-acenaphthapyridine methiodide sensitises up to λ7100 and has its maximum at λ5750. However, it is not always that the replacement of methyl radicals by ethyl radicals in cyanine dyes produces an increased sensitisation. Thus, 1:1′-dimethyl-5:6-benz-ψ-cyanine iodide sensitises up to λ6300 and has a maximum at λ5700, whereas 1:1′-diethyl-5:6-benz-ψ-cyanine iodide sensitises only up to λ6100, and has the maximum at λ5750 (Hamer, *J. Chem. Soc.*, 1928, 212).

In the compound (B) the sensitisation extension is up to λ6500 and the maxima at λ5400 and λ6000. In (C) the sensitisation extends to λ6400, and the maxima are at λ5500 and λ5950. Here there is also a faint sensitisation band at λ6800. The sensitisation spectrum of (D) is very similar to that of (C) except that in this case the sensitivity at λ6803 becomes well defined.

Fig. 1



(B) is a slightly better sensitiser than (C) which may mean that the replacement of a methyl group by an ethoxyl group in the 6′ position has not been beneficial. Of the three, (D) has the most extensive sensitisation band, and it has no substituent in the 2′ position. We therefore confirm the observation of Mills and Pope (*Phot. J.*, 1920, **60**, 198) that in this class of dyes, from the point of view of sensitising efficiency, the loading of the 2′ position is not advantageous.

Because of their close relationship, in each case the absorption spectrum of the dye is given below the sensitisation spectrum in Fig. 1. The frequencies of maximum absortion are recorded in column 8 of Table I.

The fluorescence of weak alcoholic solutions of these dyes is given in Table II (also see Jelly, *Nature*, 1936, **138**, 1009).

TABLE I

1.	2.	3.	4.		5.	6.	7.		8.
Compound.	Colour and shape.	Reflex.	Pleochroism. Position one.	Position at right ang	Rel. resist. to decolorisation.	Rel. intens. of colour in soln.	Extra sensitisation. Range	Maxima	Frequency of maximum absorption
A	Very dark sage-green crystals	Scintillating bottle-green	Amethyst	Colorless	7.28	3.33	5000—7400Å	5600 & 6600Å	57250×10^{10}
B	Greenish stunted needles	Greenish yellow	Colorless	Opaque	1.0	1.0	5100—6500	5400 & 6000	53090×10^{10}
C	Dark green needles	Golden green	Light green	Brownish green	2.08	1.42	5200—6400 faint band at 6800Å	5500 & 5950	52170×10^{10}
D	Dark felt-green crystals	Shining green	Grey	Yellownish green	1.92	1.60	5200—6550Å well defined band at 6800Å	5500 & 6000	53380×10^{10}

TABLE II

Colour of the fluorescent beam seen at right angles to the incident beam.

Wallace colour filter No.	A.	B.	C.	D.
1	Light absorbed	Light absorbed	Light absorbed	Light absorbed
2	Orange	Orange-red	Red	Orange
3	Blue violet	Violet	Blue	Blue-violet
4	Orange	Orange	Orange	Orange
5	Pink	Claret red	Red	Deep pink
6	Orange-yellow	Orange	Faint red	Faint orange
7	Faint violet	Red-violet	Violet	Violet
8	Light violet	Violet	Faint yellowish blue	Deep violet
9	Blue-violet	Pink-violet	Blue	Deep violet
10	Faint yellow	Reddish orange	Pink	Faint violet

The colours imparted to silk, wool and cotton on dyeing with these compounds are shown in Table III.

TABLE III

Compound.	Wool.	Silk.	Cotton.
A	Black	Deep red-violet	Black berry
B	Violet	Faint red-violet	Red-violet
C	Deep violet	Violet	Light violet
D	Deep chocolate	Light violet	Violet

(A) is a powerful photographic sensitiser. It was thought of interest to compare its properties with other similarly constituted cyanines. For this purpose six compounds in two sets, along with their formulae, important characteristcs and other relevant information, have been collected in Table IV. They are arranged in order of decreasing molecular weight, this having been attained by knocking out a benzene ring as we descend the series. In the bottom set additional decrease in weight has been achieved by having two methyl radicals attached to the ternary nitrogen atom instead of ethyl.

It is known that increase in the size of a cyanine dye shifts its sensitisation spectrum farther towards the red. This is true of all the cyanines under consideration. In each set, the heavier dye sensitises farther into the red than the next lighter dye.

Mills and Pope (*Phot. J.*, 1920, **60**, 256) observed that 1:1′-diethylcarbocyanine iodide is a much better sensitiser than the corresponding dimethyl compound, 1:1′-dimethylcarbocyanine iodide.

TABLE IV

Compound.	M.W.	Crystal shape.	M.p.	Absorption maximum.	Sensitisation		Reference.
					Range.	Maximum.	
2-*p*-Diethylaminostyryl-*β*-naphthaquinoline ethiodide	508	Sage-green crystals	189°	5240	3900 to 7400 Å	6600Å	(A)
2-*p*-Diethylaminostyrylquinoline ethiodide	458	Light chocolate needles	230°	...	4200 to 6400 Å	5800	(i) Doja *et al*., this *Journal*, 1943, **20**, 153 (ii) Doja and Prasad, *Patna Univ. J.*, 1945, **2**, No. 1, 6.
2-*p*-Diethylaminostyrylpyridine ethiodide	408	Vermilion-red needles	205°	...	4200 to 5750 Å	5400	(i) Doja *et al*., this *Journal* 1942, **19**, 377. (ii) Doja and Prasad, *loc. cit.*
2-*p*-Dimethylaminostyryl-*β*-naphthaquinoline ethiodide	480	Lustrous needles	228-235°	5250	3600 to 7000 Å	6200	(i) Mills and Raper, *J. Chem. Soc.*, 1925, 3473 (ii) Bloch and Hamer, *Phot. J.*, 1930, **70**, 374.
2-*p*-Dimethylaminostyrylquinoline ethiodide	430	Prisms	249°	5300	3600 to 6750 Å	4700	(i) König and Treichel, *J. prakt. Chem.*, 1921, **102**, 63. (ii) Bloch and Hamer, *loc. cit.*
2-*p*-Diethylaminostyrylpyridine ethiodide	380	Reddish violet plates	265°	4700	3600 to 6500 Å	5400	(i) Doja *et al*., this *Journal*, 1942, **19**, 125. (ii) Bloch and Hamer, *loc. cit.*

Here only among the *β*-naphthyl compounds is the diethyl derivative clearly superior to the dimethyl one. In the other cases it is not so true. The comparison of the melting points of these compounds is also not without interest. It increases with

decreasing molecular weight. Not quite the expected thing. In the bottom set it is consistently so ; in the top set the pyridine compound only is an exception, having an m. p. lower than the corresponding quinoline compound. It is also noteworthy that in every case the dimethylamino compound has a lower m.p. than the corresponding diethylamino compound, notwithstanding the heavier molecular weight of the former (cf. Doja and Banerjee, this *Journal*, 1946, **23**, 222).

EXPERIMENTAL

β-Naphthaquinaldine Ethiodide.—β-Naphthaquinaldine (1.0 g.) and ethyl iodide (0.8 g.) were heated together in a sealed tube on a water-bath for 26 hours. The yellow substance thus produced was crystallised from water and then recrystallised from alcohol, yield 1.10 g. (60.84%), m.p. 235-36°. (Found : I, 36.27. $C_{16}H_{16}NI$ requires I, 36.38 per cent).

2-Diethylaminostyryl-β-naphthaquinoline Ethiodide.—β-Naphthaquinaldine ethiodide (0.50 g.), *p*-diethylaminobenzaldehyde (0.25 g.) and piperidine (4 drops) were shaken up in a flask with 10 c.c. of alcohol. A red colour developed in the cold, which deepened on warming. The solution was refluxed for 4 hours and the dye precepitated out with ether. It was recrystallised from methyl alcohol, yield, 0.53 g. (72.8%), m.p. 139°. (Found : N, 5.74 ; I, 24.91. $C_{27}H_{29}N_2I$ requires N, 5.71 ; I, 25.0 per cent).

1 : 1′-Diethyl-2′ : 6′-dimethyl-β-naphthaisocyanine Iodide.— β-Naphthaquinaldine ethiodide (0.80 g.) and *p*-toluquinaldine ethiodide (0.74 g.) were completely dissolved in 15 c.c. of alcohol. To this was added all at once a solution of 0.1 g. of caustic potash in the smallest necessary quantity of alcohol. The colour changed from yellow to dark brown and then to deep reddish violet. The solution was refluxed for 6 hours and then left overnight at the room temperature. A few needle clusters appeared at the bottom of the flask. It was further cooled in a frigidaire for 24 hours, and the separated crystals recrystallised from ethyl alcohol, yield 0.345 g. (28.28%), m.p. 225°. (Found : N, 5.22 ; I, 23.85. $C_{29}H_{29}N_2I$ requires N, 5.26 ; I, 23.87 per cent).

1:1′-Diethyl-2′-methyl-6′-ethoxyl-β-naphthaisocyanine Iodide.—In a hot solution of β-naphthaquinaldine ethiodide (0.8 g.), 6′-ethoxyquinaldine ethiodide (0.8 g.) and alcohol (16 c.c.), was poured a strong alcoholic solution of caustic potash (0.1 g.), when the colour changed to strong violet. The contents of the flask were heated on a water-bath for 8 hours and then left to stand for 3 days. Tiny needles separated out which were carefully washed and recrystallised from ethyl alcohol, yield 0.310 g. (24.06%), m.p. 220°. (Found: N, 5.18 ; I, 22.55. $C_{30}H_{31}N_2I$ requires N, 4.98 ; I, 22.59 per cent).

1:1′-Diethyl-6′-methyl-β-naphthaisocyanine Iodide.—β-Naphthaquinaldine ethiodide (0.8 g.) and *p*-toluquinoline ethiodide (0.68 g.) were dissolved in hot alcohol (15 c.c.) to which a solution of caustic potash (0.1 g.) in a very small quantity of alcohol was added. The red solution was gently boiled for 6 hours and then slowly cooled for 24 hours. Some crystals appeared which increased on standing for another 24 hours.

These were recrystallised from ethyl alcohol, yield 0.520 g. (43.80%), m. p. 218°. (Found : N, 5.36 ; I, 24.48. $C_{28}H_{27}N_2I$ requires N, 5.40 ; I, 24.51 per cent).

The yield and melting points given above are all those of twice recrystallised specimens.

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FRIEDEL AND CRAFTS ACETYLATION OF METHYL β-RESORCYLATE AND FRIES MIGRATION OF METHYL 2-HYDROXY-4-ACETOXYBENZOATE IN PRESENCE OF BORON TRIFLUORIDE

By P. L. Trivedi

Equimolecular proportions of methyl β-resorcylate and acetic anhydride have been condensed in presence of boron trifluoride etherate (2 mols.) to yield β- and γ-isomers of the products, methyl 2:4-dihydroxy-5-acetyl- and -3-acetyl-benzoate respectively. Fries migration of methyl 2-hydroxy-4-acetoxybenzoate in presence of (1) boron trifluoride etherate and (2) $AlCl_3$ afforded β- and γ-isomers, yields in both the cases being almost the same as in the case of the acetylations.

In an earlier paper (this *Journal*, 1951, **28**, 245) it was reported that in the Friedel and Crafts acetylation of methyl β-resorcylate in presence of aluminium chloride, methyl 2:4-dihydroxy-3-acetylbenzoate was formed in considerable quantity along with 2:4-dihydroxy-5-acetylbenzoate. The same acetylation has been attempted in presence of boron trifluoride etherate.*

Considerable work has been carried out on the Friedel and Crafts alkylation in the presence of boron trifluoride, but only a few instances are known of acylation in its presence. Anisole (Meerwein, *Ber.*, 1933, **66**, 411; Meerwein and Vossen, *J. prakt. Chem.*, 1934, **141**, 149), phenol ("Newer Methods of Preparative Organic Chemistry", Interscience Publishers, Inc., New York, 1948, p. 281), resorcinol (Killeler and Lindwal, *J. Amer. Chem. Soc.*, 1948, **70**, 428) etc. have been acetylated and the corresponding ketones obtained.

In the present work equimolecular proportions of methyl β-resorcylate and acetic anhydride (1 mol.) have been condensed in presence of boron trifluoride etherate (2 mols.) by heating on a steam-bath for 2 hours, affording in good yield both the β- and γ-isomers, viz , methyl 2:4-dihydroxy-5-acetyl- and- 3-acetylbenzoate respectively. Use of 3 mols. of boron trifluoride etherate did not increase the yield of either the β- or the γ-isomer. The yields are almost the same as those obtained in the case of aluminium chloride. Acetyl chloride was substituted in place of acetic anhydride and the reaction was carried out at room temperature and at 120°; under the former condition the reaction proceeded to a very limited extent and the yield was very poor. The yields of the β- and γ-isomers in case of the acetylation at 120° were almost the same as those in the case of acetic anhydride.

* Kindly supplied by the Organic Division of the National Chemical Laboratory of India.

In view of the interesting results obtained in the Friedel and Crafts acetylation it was also thought of interest to study the Fries migration of methyl 2-hydroxy-4-acetoxybenzoate in presence of boron trifluoride etherate (2 mols.) and aluminium chloride (2 mols.) in nitrobenzene. The reaction mixture was worked up as before. The yields of the β- and γ-isomers in both the cases were almost the same as those obtained in the Friedel and Crafts acetylation.

Though the use of boron trifluoride in place of aluminium chloride in the above reactions does not improve the yields, the reaction proceeds smoothly and the reaction mixture gives clean products.

Experimental

Acetylation of Methyl β-Resorcylate in presence of Boron Trifluoride.—Boron trifluoride etherate (14.4 g., 2 mols.) was added to a mixture of anhydrous methyl β-resorcylate (8.4 g., 1 mol.) and acetic anhydride (5 g., 1 mol.). The reaction mixture was refluxed on a steam-bath for 2 hours, poured in cold water while hot and subjected to steam distillation, when a white product distilled over with steam. It was collected and dried. The dried product (3 g., m. range 60°-90°) was thoroughly powdered and shaken with cold petroleum ether (b. p. 40°-60°, 30 c.c.) and filtered. The insoluble portion was crystallised from alcohol in stout needles, m.p. 122-23°, yield 1.6 g. Mixed melting point with methyl 2:4-dihydroxy-5-acetylbenzoate, prepared by using aluminium chloride (*loc. cit.*), was not depressed.

The product obtained on removal of petroleum ether was crystallised from alcohol in long wooly needles (0.6 g.), m.p. 83-84°. Mixed melting point with methyl 2:4-dihydroxy-3-acetylbenzoate, prepared by using aluminium chloride (*loc. cit*), was not depressed.

Methyl 2-Hydroxy-4-acetoxybenzoate.—A mixture of methyl β-resorcylate (16.8 g.), acetic anhydride (10 c.c.) and sodium acetate (5 g.) was heated on a steam-bath for 5 hours. It was then poured on crushed ice when a pasty product was obtained. After filtering and washing with ice-cold water it was treated with ice-cold sodium hydroxide solution (2%) and filtered. The filtrate on acidification with cold hydrochloric acid gave a pasty mass which after drying was crystallised from alcohol (by keeping the saturated solution overnight in a refrigerator) in long needles (8 g.), m.p. 53-55°. (Found: C, 57.2 ; H, 4.5. Calc. for $C_{10}H_{10}O_5$: C, 57.1; H, 4.7 per cent). It gave wine-red coloration with alcoholic ferric chloride.

Fries Migration of Methyl 2-Hydroxy-4-acetoxybenzoate in presence of (i) Boron Trifluoride Etherate and (ii) Aluminium Chloride.—(*i*) Boron trifluoride etherate (14.4 g., 2 mols.) was added to methyl 2-hydroxy-4-acetoxybenzoate (10 g., 1 mol.) and heated on a steam-bath for 2 hours under reflux. The reaction mixture after pouring in cold water was subjected to steam distillation when a white product with a melting range 60°-90° distilled. It was worked up as before with petroleum ether (40°-60°). The yields of the β- and γ-isomers were 1.4 g. (m.p. 122-23°) and 0.55 g. (m.p. 83-84°) respectively.

(ii) A solution of methyl 2-hydroxy-4-acetoxybenzoate (10 g., 1 mol.) in dry nitrobenzene (20 c.c.) was added to a solution of anhydrous aluminium chloride (13.4 g., 2 mols.) in nitrobenzene (50 c.c.). The reaction mixture was heated in an oil-bath at 160°-170° for 3 hours. After cooling ice-cold dilute hydrochloric acid was added and the reaction mixture subjected to steam distillation. After the nitrobenzene had distilled over completely, the distillation was continued further when a white product with melting range 60°-90° steam distilled. It was collected and worked up with petroleum ether (40°-60°) as before. The yields of the β- and the γ-isomers were 1.4 g. (m.p. 122-33°) and 0.6 g. (m.p. 83-84°) respectively.

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CHEMISTRY OF RARE EARTHS. PART X. UROTROPIN AND ANTIPYRINE COMPLEXES OF THIOCYANATES AND DITHIONATES OF RARE EARTHS

By Nihar Kumar Dutt and Hari Gopal Mukherjee

Preparation and properties of complexes of rare earth thiocyanates and dithionates with urotropin and antipyrine have been described.

Rare earth nitrates have been known to give beautiful crystalline compounds with urotropin (Barbieri and Calzolari, *Atti. R. Acad. Lincei*, 1911, v, **20**, 164) and antipyrine (Kolbe, *Z. anorg. Chem.*, 1913, **83**, 143). Similar compounds with rare earth perchlorates, iodides and nitrites have been isolated By Wilke-Dorfurt and Schliephake (*ibid.*, 1928, **170**, 123) and others. One of the authors (N. K. D.) has isolated several compounds of rare earth thiosulphates with urotropin and antipyrene. Preparation and properties of similar complexes of urotropin and antipyrene with rare earth (La, Ce, Pr) thiocyanates and dithionates form the subject matter of the present communication. Simple rare earth thiocyanates and dithiocyanates have long been known in the solid state as highly soluble and hygroscopic salts. These complexes, however, are of moderate solubility and not hygroscopic, and have been obtained as beautiful shining crystals.

Experimental

Purification of Rare Earth Salts used as Starting Material: (*a*) *Lanthanum salt* used as the starting material was double ammonium nitrate, obtained through the courtesy of Sociètè des Produits, Chemique de Terre Rares as a free gift. It was purified by conversion into anhydrous sulphate which was then dissolved in ice-water and heated to 33°, when hydrated lanthanum sulphate ($9H_2O$, hexagonal) was obtained pure, being not isomorphous with hydrated praseodymium sulphate ($8H_2O$, monoclinic), the impurity present in it.

(*b*) *Cerium salt* was extracted from monazite sand by the classical ceric ammonium nitrate method. It was further purified by several recrystallisations of the salt from concentrated nitric acid.

(*c*) *Praseodymium salt* was obtained from Mss. Frankel and Landau. It is liable to contain little lanthanum. It was purified by fractional crystallisation of the nitrate. Lanthanum accumulated in the solution and pure praseodymium salt precipitated first.

Lanthanum-urotropin Thiocyanate.—Lanthanum nitrate (5 g.) was dissolved in the least quantity of water, cooled, and to this was added dropwise urotropin (6 g.), also dissolved in the least quantity of cold water. Separated crystals of lanthanum-urotropin nitrate were dissolved in the least quantity of cold water, added dropwise. The clear solution was then filtered and to the filtrate was then added a saturated solution ammonium thiocyanate containing 5 g. of the solid when the complex salt separated

as beautiful shining microcrystals. These crystals were filtered under suction and washed carefully with ice-cold water.

The compound is white, microcrystalline and moderately soluble in water. It is more soluble in hot water than in the cold. The solution gradually decomposes giving lanthanum hydroxide. It melts at 250°-55° with decomposition. Its solubility in water at 35° = 15.48 g. in 100 c. c. of the solution. [Found: La, 18.76, 19.01; S, 12.77, 13.18; N, 21.10, 20.88. $La(SCN)_3 . 2C_6H_{12}N_4 . 8H_2O$ requires La, 18.86; S, 13.10; N, 20.89 per cent].

Cerous-urotropin thiocyanate was formed when a mixture of cerous nitrate (5 g.) and urotropin (6 g.) was treated with a saturated solution of ammonium thiocyanate.

It resembles the previous salt in all respects, m.p., 255-59° (decomp.), solubility at 35° = 11.25 g./100 c. c. [Found: Ce, 18.56, 19.12; S, 13.14, 13.12; N, 20.95, 20.78. $Ce(SCN)_3 . 2C_6H_{12}N_4 . 8H_2O$ requires Ce, 18.97; S, 13.00; N, 20.86 per cent].

Praseodymium-urotropin thiocyanate was also prepared in an analogous way to the other two salts using praseodymium nitrate as the starting material. The compound is light green. In all other respects it resembles the previous compounds. It melts at about 260° with decomposition. Solubility at 35° = 8.67 g./100 c.c. [Found: Pr, 18.88, 19.28; S, 12.88, 13.25; N, 21.21, 20.78. $Pr(SCN)_3 . 2C_6H_{12}N_4 . 8H_2O$ requires Pr, 19.08; S, 13.00; N, 20.84 per cent].

Lanthanum-hexa-antipyrene Thiocyanate.—To a concentrated solution of lanthanum nitrate (3 g.) was added an aqueous solution of antipyrene (5 g.). The crystals separating were dissolved in the least quantity of cold water, added dropwise. To this solution was then added dropwise a saturated solution of ammonium thiocyanate when beautiful colorless crystals separated. It was filtered under suction, washed with ice-cold water twice and dried between folds of filter paper.

The compound is colorless and crystalline in nature, moderately soluble in water but less so than the corresponding urotropin compound. An aqueous solution decomposes on heating. It melts at 270° with decomposition leaving a black residue. Solubility at 35° = 13.67 g./100 c.c. [Found: La, 9.76, 9.58; S, 6.72, 6.75; N, 14.64, 14.71. $La(SCN)_3 . 6C_{11}H_{12}N_2O$ requires La, 9.64; S, 6.66; N, 14.51 per cent].

Cerous ^{III}-hexa-antipyrene thiocyanate was prepared in the same way as described above substituting cerous nitrate for lanthanum nitrate. It resembles the previous compound in almost all respects. It melts at about 270-72° with decomposition; solubility at 35° = 10.52 g./100 c.c. [Found: Ce, 10.01, 9.88; S, 6.78, 6.71; N, 14.54, 14.66. $Ce(SCN)_3 . 6C_{11}H_{12}N_2O$ requires Ce, 9.77; S, 6 65, N, 14.51 per cent].

Praseodymium-hexa-antipyrene thiocyanate was prepared in an analogous manner using praseodymium nitrate. It is light green in colour. It melts at 274-76° leaving a black residue. Solubility at 35° = 7.48 g./100 c.c. [Found: Pr, 9.89, 9.66; S, 6.78, 6 85; N, 14.50, 14.63. $Pr(SCN)_3 . 6C_{11}H_{12}N_2O$ requires Pr, 9.77; S, 6.65; N, 14.57 per cent].

Lanthanum-urotropin Dithionate.—To a concentrated solution of lanthanum nitrate (5 g.) in cold water was added an aqueous solution of urotropin (10 g.) and the solution was filtered from any precipitate. To this solution was then added a saturated solution

of sodium dithionate dropwise when beautiful white crystals separated which were left for sometime and then filtered under suction. The crystals were washed with ice-cold water and recrystallised from least quantity of cold water, yield 7.5 g.

The compound is colorless and crystalline. It is moderately soluble in water, much less than the lanthanum dithionate itself which has been described as highly soluble by Cleve. It melts at about 260° with decomposition. Solubility at 35° = 6.58 g./100 c.c. [Found: La, 17.25, 17.46 ; S, 12.22, 12.18 ; N, 21.18, 21.18. $La_2(S_2O_6)_3 . 6C_6H_{12}N_4$ requires La, 17.39 ; S, 12.01 ; N, 21.03 per cent].

Cerous ^{III}*-urotropin dithionate* was prepared in the same way, using cerous nitrate. Its properties resemble the other salt in many respects. It melts at about 262° with decomposition. Solubility at 35° = 5.02 g./100 c.c. [Found: Ce, 17.75. 17.68 ; S, 12.16, 12.32 ; N, 21.32, 21.15. $Ce_2(S_2O_6)_3 . 6C_6H_{12}N_4$ requires Ce, 17.5 ; S, 12.00; N. 21.0 per cent].

Praseodymium-urotropin dithionate was prepared similarly using praseodymium nitrate. The compound separates in beautiful green crystals. In other respects it resembles the corresponding lanthanum and cerium salts. Solubility at 35° = 3.35 g./100 c.c. [Found: Pr, 17.85, 17.67 ; S, 12.08, 12.18 ; N, 21.16, 21.02. $Pr_2(S_2O_6)_3 . 6C_6H_{12}N_4$ requires Pr, 17.60; S, 11.98 ; N, 20.97 per cent].

Lanthanum-hexa-antipyrene dithionate was similarly prepared from lanthanum nitrate, antipyrene and sodium dithionate. The compound separated in colorless beautiful crystals. Unlike the simple dithionate of lanthanum, the solubility of the complex is very low. It does not melt at any definite temperature and decomposes on heating. Solubility at 35° = 1.68 g./100 c.c. [Found: La, 14.88, 14.36; S, 10.36, 10.28 ; N, 9.12, 8.88. $La_2(S_2O_6)_3 . 6C_{11}H_{12}N_2O$ requires La, 14.74; S, 10.18; N, 8.91 per cent].

Cerous ^{III}*-hexa-antipyrene Dithionate.*—The method of preparation is identical as the previous compound. Solubility at 35° = 1.12 g./100 c.c. [Found: Ce, 15.02; S, 10.36 ; N, 8.86. $Ce_2(S_2O_6)_3 . 6C_{11}H_{12}N_2O$ requires Ce, 14.83; S, 10.17; N, 8.90 per cent].

Praseodymium-hexa-antipyrene dithionate was obtained in the same way as the cerrous ^{III} complex. The salt separated as beautiful green shining crystals. Solubility at 35° = 0.94 g./100 c.c. [Found: Pr, 15.08; S, 10.42; N, 8.78. $Pr_2(S_2O_6)_3 . 6C_{11}H_{12}N_2O$ requires Pr, 14.92; S, 10.16; N, 8.89 per cent].

Method of Analysis.—Sulphur was estimated as barium sulphate after oxidation with nitric acid and bromine and separation of rare earth from this solution with ammonia. Rare earth was estimated by dissolving this precipitate in hydrochloric acid and then reprecipitating as oxalate and subsequent ignition to oxide. Nitrogen, in urotropn compounds, was estimated after decomposition with concentrated sulphuric acid, and distillation with caustic soda, absorbing the evolved ammonia in standard acid and titrating back the excess acid with standard alkali. Nitrogen, in antipyrene complexes, was determined by Duma's method of combustion.

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CHEMISTRY OF RARE EARTHS. PART XI. UROTROPIN AND ANTIPYRENE COMPLEX OF TETRATHIONATES OF RARE EARTHS

By Nihar Kumar Dutt and Nityananda Goswami

Preparation and properties of complexes of La, Ce and Pr tetrathionates with urotropin and antipyrene have been described

Dutt and his co-workers described the preparation and properties of several urotropin and antipyrene complexes of rare earth thiosulphates (this *Journal*, 1951, **28**, 533) and dithionates (this *issue*, p. 272). Rare earth dithionates have long been known as highly soluble hygroscopic salts with several molecules of water of crystallisation. Gadolinium salts as described by Sarkar (*Ann. chim.*, 1927, *x*, **8**, 239) was so hygroscopic that it could not be analysed. Tetrathionates have not been described. We also failed to prepare the tetrathionates of rare earths, sample being highly soluble and refusing to crystallise. As the solubilities of the dithionates are much diminished by combination with urotropin and antipyrene, their isolation is easier Similar behaviour with rare earth tetrathionates was expected, and isolations of the tetrathionates of rare earths in combination with urotropin and antipyrene have been made with success.

Experimental

Purified rare earth salts, which had been used in Part X (*loc. cit.*) of this series, were employed in the following preparations.

Lanthanum-urotropin Tetrathionate.—To a concentrated solution of lanthanum nitrate (5 g.) in cold water was added an aqueous solution of urotropin (10 g.) and the solution was filtered from any precipitate. To this solution was then added a saturated solution of sodium tetrathionate dropwise, when beautiful white crystals separated. These were left for sometime, and filtered under suction. The crystals were washed with ice-cold water and recrystallised from least quantity of cold water.

The compound is colorless and crystalline. It is moderately soluble in water. The salt is quite stable in the solid state and in aqueous solution in the cold. An aqueous solution of the salt decomposes on heating with separation of sulphur and lanthanum hydroxide. It melts above 250° with decomposition. [Found: La, 18.31, 18.42; S, 25.73, 25.48; N, 14.71, 14.61. $La_2(S_4O_6)_3.4C_6H_{12}N_4$ requires La, 18.41; S, 25.43; N, 14.83 per cent].

Cerous ^{III}*-urotropin tetrathionate* was prepared in the same way as the lanthanum salt using cerous nitrate. In properties it resembles the previous salt in all respects. [Found: Ce, 18.32, 18.65; S, 25.56, 25.48; N, 14.72, 14.54. $Ce_2(S_4O_6)_3.4C_6H_{12}N_4$ requires Ce, 18.52; S, 25.40; N, 14.81 per cent].

Praseodymium-urotropin tetrathionate was prepared in the same way as the above mentioned compound using praseodymium nitrate. The salt separated in beautiful

green crystals. In other respects it resembles the other salts. [Found: Pr, 18.52, 18.68; S, 25.56, 25.37; N, 14.92, 14.82. $Pr_2(S_4O_6)_3 . 4C_6H_{12}N_4$ requires Pr, 18.61; S, 25.34; N, 14.79 per cent].

Lanthanum-hexa-antipyrene Tetrathionate.—To a concentrated solution of lanthanum nitrate (3 g.) was added cold aqueous solution of antipyrene (5 g.). Crystals separated, if any, were dissolved in the least quantity of cold water and filtered. To this filtered solution was then added dropwise a cold saturated solution of sodium tetrathionate when beautiful colorless crystals separated. It was filtered under suction, washed with ice water and dried first between folds of filter paper and finally in air.

The compound is colorless and crystalline. It is moderately soluble in water and quite stable in the solid state for several days. [Found: La, 13.62, 13.45; S, 18.58, 18.65; N, 8.22, 8.18. $La_2(S_4O_6)_3 . 6C_{11}H_{12}N_2O$ requires La, 13.38; S, 18.48; N, 8.08 per cent].

Praseodymium hexa-antipyrene tetrathionate was prepared in an identical manner as the previous compound. Its properties are very similar to the latter. [Found: Pr, 13.72, 13.39; S, 18.46, 18.58; N, 8.21, 8.12. $Pr_2(S_4O_6)_3 . 6C_{11}H_{12}N_2O$ requires Pr, 13.45; S, 18.44; N, 8.07 per cent].

Method of Analysis.—Sulphur was estimated as barium sulphate after oxidation with alkali and bromine and after separation of rare earth from this solution with ammonia. Rare earths and nitrogen, in urotropin complexes, were estimated as shown in Part X (*loc. cit.*). Nitrogen in antipyrene compounds was estimated by Duma's method of combustion.

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STUDIES ON THE ADSORPTION FROM NON-AQUEOUS SOLVENTS. PART III

By A. C. Chatterji and R. D. Srivastava

Adsorption of two more solutes—cinnamic acid (polar) and phenanthrene (non-polar), in both polar and non-polar solvents has been studied. The changes in the amounts adsorbed from different solvents have been explained on the basis of differences in the internal pressures of solute and solvent. It has been observed that since in a solution consisting of two components, where exists a difference in the internal pressure, the escaping tendencies change, and hence, adsorption also changes. The change increases with the difference and may be positive or negative. It is positive when the solute has a lower internal pressure than the solvent, and negative, when higher. Deviations from the rule occur due to polarity. The adsorption of naphthalene, phenanthrene, benzoic acid and cinnamic acid increases with the increase in the difference, in the solvents having higher internal pressures. But the increase is less marked in acids due to their polarity. The adsorption of naphthalene and phenanthrene decreases with the increase in the difference, in the solvents having a lower internal pressure, but of acids under the same conditions increases, which has been explained due to their polarity.

In previous communications (this *Journal*, 1951, **28**, 315; 1952, **29**, 327) adsorption of polar and non-polar substances from both types of solvents was studied, and the changes in the adsorption from solvent to solvent were accounted for on the basis of changes in the polarity, solubility, surface tension, and the effect of the latter on solubility. In the present paper work has been extended to more solutes, and the changes in the adsorption has been explained on the basis of differences in the internal pressures.

It is known that the internal pressure of a substance is a measure of the attractive force between the molecules. If accumulation in an interface is considered as a manifestation of the escaping tendency of the solute from the solution phase, then with the difference in the internal pressures adsorption will also change as the escaping tendency changes. The substance having a greater escaping tendency will tend to be adsorbed to a greater extent which will be subsequently determined by the difference in the internal pressures.

Taking this point into consideration, an attempt has been made in this paper to correlate the changes in adsorption from different solvents with the differences in the internal pressures.

Experimental

All the chemicals used herein were purified by standard methods. Experimental method was the same as given in Parts I and II of the series (*loc. cit.*). The values of adsorption at one concentration are given in Table I and at other concentrations in Tables II and III. The adsorbed amounts of benzoic acid and naphthalene obtained from the previous work (*loc. cit.*) have also been included for showing the validity of the relationship in these cases also. The values of internal pressures from solubility data have been reproduced in column 2 from Mortimar (*J. Amer. Chem. Soc.*, 1923, **45**, 633). In column 3, calculated values of relative internal pressures from heat of vaporisation

and molecular volumes of liquids are given using Hildebrand's equation (*ibid.* 1919, **41**, 1067).

TABLE I

Solvent.	Relative internal pressure.		Adsorption in m. moles/litre at concentration of			
			Naphthalene. (0.2 *M*)	Phenanthrene (0.5 *M*)	Benzoic acid. (0.5 *M*)	Cinnamic acid. (0.5 *M*)
1.	2.	3.	4.	5.	6.	7.
CCl_4	0.84	0.847	9.30	23.0	103.3	80.2
$C_6H_5CH_3$	0.93	0.875	12.10	26.7	53 7*	70.0
C_6H_6	0.94	0.936	15.5	31.0	66.9	68 2
C_6H_5Cl	0.98	0.986	9.6*	40.5	38.0	58.0
CH_3COCH_3	1.32	1.030	27.6	44.0	42.3	30.9
CH_3COOH	1.95	1.044	21.2	47.2	—	—
n-BuOH	—	1.046	28.2	47.2	49.6	38.0
n-PrOH	—	1.210	31.1	55 0	49.8	39 7
EtOH	2.90	1.423	41.7	58.9	51.0	42.0
MeOH	3.35	1.940	45.6	64.7	51.3	45.6
Naphthalene	1.00	1.000	—	—	—	—
Benzoic acid	1.38	1.010	—	—	—	—
Phenanthrene	1.02	1.006	—	—	—	—
Cinnamic acid	—	0.994	—	—	—	—

*Are irregularities.

TABLE II

Temp. = 30°

Solvent.	Adsorption of phenanthrene in m. moles/litre at concentration							
	0.7*M*.	0.6*M*.	0.5*M*.	0.4*M*.	0.3*M*.	0.2*M*.	0.1*M*.	0.05*M*
CCl_4	26.7	24.9	23.0	21.1	19.0	17.1	14.9	12.1
$C_6H_5CH_3$	31.5	29.1	26.7	24.0	21.5	18.9	16.2	12.3
C_6H_6	36.6	34.0	31.0	28.1	25.0	21.8	18.0	13.2
C_6H_5Cl	48.1	44.8	40.5	36.0	31.1	26.1	21.0	15.2
CH_3COCH_3	53.2	49.0	44.0	39.1	34.0	29.0	22.8	17.0
CH_3COOH	56.0	51.9	47.2	42.0	36.2	30.3	24.0	17.0
n-BuOH	59.9	55.8	51.3	46.5	41.0	35.0	27.7	19.0
n-PrOH	63.1	59.0	55.0	50.8	44.8	37.5	29.0	19.0
EtOH	65.3	62.1	58.9	54.0	47.9	40.7	32.0	22.0
MeOH	74.1	70.0	64.7	59.0	52.2	42.5	33.5	23.0

TABLE III

Temp. = 30°

Solvent.	Adsorption of cinnamic acid in m moles/litre at concentration						
	0.6 *M.*	0.5 *M.*	0.4 *M.*	0.3 *M.*	0.2 *M.*	0.1 *M.*	0.05 *M.*
CCl_4	—	80.2	71.4	60.4	46.1	27.4	10.9
$C_6H_5CH_3$	79.8	71.0	61.9	51.4	38.2	21.2	10.1
C_6H_6	76.1	68.2	59.0	49.0	36.6	21.2	10.1
C_6H_5Cl	64.6	58 0	50.8	41.7	31.6	18.9	9.4
MeOH	51.1	45.6	38.9	31.3	23.1	13.1	9.0
EtOH	47.6	42.0	35.8	29.3	22.2	12 9	9.0
n-PrOH	43.5	39.7	34.3	28.2	21.0	12.8	9.0
n-BuOH	42.0	38.0	33.0	27.1	21.0	12.6	9.0
CH_3COCH_3	32.2	30.9	28.7	24.9	20.0	13.5	9.5

DISCUSSION

Consider a mixture of two components A and B : if the forces between molecules of A are almost the same as those between molecules of B, and neither type of molecule has any polarity resulting in an external electric field, then the forces between A and B will also be the same. Under these conditions the average force acting on any molecule will be independent of composition, and escaping tendency will be normal, hence adsorption will also be normal. From Table I it is seen that the adsorption of all the substances is approaching the normal value in those solvents which have nearly the same internal pressure as the solute.

If, on the other hand, the forces between the molecules of A are greater than those between the molecules of B, the former will tend to aggregate together so that the latter are squeezed out ; in other words, the high internal pressure of one of the components of the mixture increases the escaping tendency of the other, and hence, adsorption. For the same reason adsorption of naphthelene and phenanthrene, benzoic and cinnamic acid increases with the increase in the difference of internal pressure in the solvents which have a higher internal pressure than these solutes. The decrease in the adsorption of naphthalene and phenanthrene in the solvents of low internal pressure is also due to the same reason, because in these cases escaping tendency of the solvents is increased as they have a lower internal pressure.

If the component A is polar, that is, it has an unsymmetrical field of force and contains a grouping possessing an appreciable dipole moment, then there is a specific attraction between the molecules which tends to decrease their external electrostatic field. Under these conditions the escaping tendency of a polar compound in non-polar solvents is increased more than that indicated by the direct proportionality to the

differences in the internal pressure. For this reason adsorption of benzoic and cinnamic acids increases in non-polar solvents.

In the extreme case of attraction between both polar molecules, attraction between A and B becomes abnormally large, and hence, in such cases escaping tendencies and adsorption of each species are more reduced than that indicated by the difference in the internal pressure and therefore, increase is not very much marked in the adsorption of acids from polar solvents.

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CHROMATOGRAPHIC ESTIMATION OF SMALL AMOUNTS OF PHOSPHATES

By M. A. Rangarajan, C. N. Venkatachallam and B. S. Srikantan

A chromatographic method of estimating phosphates in small quantities has been developed and used in the estimation of P_2O_5 in bone ash.

Briggs (*J. Biol. Chem.* 1922, **53**, 13) has described a colorimetric method of estimating inorganic phosphates in urine by the blue colour produced in 30 minutes by the phosphomolybdate hydroquinone complex. This method did not give concordant results with the ends of samples of bone matter under ossification in normal and abnormal (dwarf) human foetus, since (*i*) in dilute solutions the blue colour of the complex was difficult to match with the standard quite sharply, and (*ii*) the reaction was not completed in 30 minutes, and in concentrated solutions the depth of the colour was produced much more rapidly. Hence, a chromatographic method of estimating P_2O_5 content of bone ash has been developed and adopted. Schwab and Dattler (*Z. angew. Chem.*, 1937, **50**, 691) have shown that anions can be separated into zones of chromatographic order and PO_4''' takes the first place among these anions. Preliminary experiments have shown that the alumina, buffered to p_H 5.4, yields good chromatograms.

Experimental

Alumina of $-90+120$ mesh was prepared as previously (this *Journal*, 1949, **26**, 415) and dried at 170° for 4 hours.

The column was formed in tubes of uniform bore of 3.4 mm. The tubes were drawn off to a tapering end and were plugged with cotton wool. The tubes were first filled with a buffer solution of p_H 5.4 (made from 50 c.c, of potassium hydrogen phthalate +5.5 c.c. $M/5$ NaOH and made up to 200 c.c.). The dry alumina of mesh $-90+120$ was added in small quantities at a time. This method was found to give a well packed column without any air bubbles being entrapped. The tubes so filled were placed in jars containing the buffer solution and left overnight before use. These columns were allowed to drain and used immediately for chromatograms.

Measured quantities of phosphate solutions were passed through the column. The adsorbed column was washed three or four times with distilled water and the nitro-ammonium molybdate solution was used as a developer. A fine yellow chromatogram with sharp edges was produced. As the developer descended, the yellow complex, composed of large sized molecules, rendered its passage rather difficult and slow. A gentle suction was helpful in such cases though the last step took a few hours. The chromatograms were regular and uniform and the results were reproducible.

Evaluation of the Constant $(1/n)$ *in the Adsorption Isotherm*

It has been pointed out in the previous paper (*loc. cit.*) that for each ion and the chromatographic tube the value of $1/n$ in Freundlich's isotherm has to be found out.

For different concentrations of the same ion, we have

$$(c_1/c_2)^{1/n} = h_2/h_1$$

where c_1 and c_2 are different concentrations of the ions and h_1 and h_2 are their respective chromatographic heights, produced by them. 0.2 c.c. and sometimes 0.4 c.c. of each of the two solutions of sodium phosphate (pure crystals analysed to Na_3PO_4, $12H_2O$) were passed through the columns in the separate tubes; the column was washed with water and developed with 0.2 to 0.4 c.c. of nitroammonium molybdate solution. The following table contains the data.

TABLE I

	1. Solution 149.5 mg. of P_2O_5/100 c.c.		2. Solution 294.5 mg. of P_2O_5/100 c.c.	
Vol. (c.c.) ...	0.2	0.4		0.2
Length (mm.) ...	5.0	10		10.0

Hence, $\left[\frac{149.5}{294.5}\right]^{-\frac{1}{n}} = \frac{10}{5}$

or $-1/n = 1.023$

Estimation of P_2O_5 *in the Samples of Bones.*—The samples of bones were carefully ashed in a weighed platinum crucible and weighed. The ash was dissolved in dilute nitric acid and the solution made up to 100 c.c., 0.5 c.c. aliquots of which were chromatographed and the results obtained are recorded in Table II. Each experiment was repeated at least thrice; averages of values not differing by more than 1 mm. were taken. The value of $1/n$(-1.023) was used to calculate the P_2O_5 content in each sample. Allowance had been made for the fact that the reference chromatogram was with 0.2 c.c. of solution, whereas here 0.5 c.c. was used.

Since 0.5 c.c. was used, the proportionate heights from table were taken as the height of chromatogram was proportional to the volume of the solution used at the same concentration.

The last column gives the data by the colorimetric method, under the best of conditions.

TABLE II

Sample No.	Height of chromatogram.	P_2O_5 in 100 c.c.	Ash.	% P_2O_5 in ash. A.	B.
N_1	2.0 mm.	26.04 mg.	62.0 mg.	41.91	44.30
N_2	10.8	130.0	335.0	39.46	34.01
N_4	15.0	177.9	476.0	37.37	45.63
AN_1	8.5	103.5	516.0	20.06	24.18
AN_4	16.5	194.8	782.0	24.91	29.73
AN_5	2.0	26.04	70.0	37.20	—

A—Chromatographic method.
B—Colorimetric method (*loc. cit.*)

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INTERFACIAL TENSION OF ALIPHATIC ESTERS WITH SURFACE ACTIVE AGENTS. PART II

By Miss Hemlata J. Kazi and C. M. Desai

The interfacial tension measurements of some aliphatic esters have been carried out against aqueous soap solutions. A number of esters, e.g. propyl, butyl and amyl acetates etc. show an exceptional behaviour in a sense that the tension increases to a sharp maximum initially with increasing soap concentration in dilute solutions, followed by a great lowering and thereafter reaching a limiting value.

In Part I of this series (this *Journal*, 1953, **30**, 209) the authors reported the unusual behaviour of hexyl and *sec.*-octyl alcohols as regards the increase of interfacial tension over a certain low range of soap concentration. This behaviour is particularly marked with a class of aliphatic esters, viz, ethyl, *iso*propyl, *n*-butyl, *iso*butyl, *iso*amyl acetates, ethyl acetoacetate and ethyl *iso*valerate; while methyl acetate and diethyl malonate do not exhibit such a behaviour.

Experimental

The interfacial tension measurements were carried out by the method described in Part I (*loc. cit.*) using sodium and potassium oleate, sodium and potassium stearate, sodium chloride and acetate, and saponin. In case of methyl and ethyl acetates, which are partly miscible with water, if the syringe is filled with ester, the liquid forms a continuous stream in the water phase, instead of drops. Since the proportionate solubility of water in the esters is considerably less than that of esters in water, when water is filled in the syringe, water forms drops at the tip in the ester phase. In this way the interfacial tension of esters against water was determined. The substances were either of standard quality or prepared by the usual method and subsequently purified before use. The results are expressed in Tables I—III and Figs. 1 and 2.

The interfacial tension against water in the ester series is found to be in the following order: methyl $<$ ethyl $<$ *iso*propyl $>$ *n*-butyl $>$ *iso*butyl $>$ *iso*amyl. It appears to be increasing first and then decreasing with the length of the aliphatic chain.

It is also obvious that the extent of the lowering of surface tension by the soap solution depends on its magnitude against water, but *iso*propyl acetate is an exception, where the relative lowering is much less. In case of all esters, except methyl acetate and diethyl malonate, the interfacial tension increases with increasing soap concentration up to 2×10^{-3} *M* and then diminishes with further increase in the soap concentration, till the limiting value is reached (Table I, Figs. 1 and 2). With saponin, however, it appears to decrease with increasing saponin concentration over the entire range, till the limiting value is reached (Table II). The interfacial tension measurements with *iso*amyl acetate using sodium chloride and sodium acetate, indicate that the tension initially increases with increase in electrolyte concentration and then diminishes with further increase in

electrolyte concentration (Fig. 2). The measurements with *n*-butyl acetate using potassium oleate-neutral, acidic and alkaline-, sodium and potassium staerate show the analogous behaviour (Table III). In general, the interfacial tension depression, follow-

TABLE I

Interfacial tension (dynes/cm.).

Na-oleate ($M \times 10^{-3}$).	Methyl acetate.	Ethyl acetate.	*iso*Propyl acetate.	*n*-Butyl acetate.	*iso*Butyl acetate.	*iso*Amyl acetate.	Ethyl acetoacetate.	Ethyl *iso*-valerate.	Diethyl malonate.
0.000	3.099	6.640	13.93	13 88	13.22	12.11	2.701	18.14	13.03
0.246	2.845	7.119	14.02	18.01	13.89	12.82	3.038	19.32	9.333
0.492	2.735	7 230	14.21	18.35	14.40	13.32	2.789	21.31	8.654
0.984	—	—	14.56	18.57	—	11.41	2 649	22.83	7.352
1.476	—	—	15.24	19.31	12.95	10 17	—	—	—
1.968	2.494	7.389	14.42	18.92	—	9 353	2.562	18.65	6.771
2.460	—	—	14.03	17.09	—	8.847	2.345	14.90	6 506
2.950	—	—	13.72	15.68	9.24	8 023	—	14.06	—
3.936	2.275	7.168	—	—	—	—	—	—	—
4.920	2.177	6.060	13.41	9 71	7.34	7.415	2.214	12 43	6.243
6 560	—	5.421							
9.800	—	—	13.32	6.715	—	5.371	2.045	8.134	5.449
14.79	—	—	13.32	6.477	5.94	—	—	6.691	—
19.68	—	—	13.12	6.183	—	5.1 8	1.635	6.092	—
29.52	—	—	13.03	5.247	5.36	4.537	—	—	—
32.80	—	—	—	—	4.74	4.319	1.296	5.283	4.455
49.20	—	—	12.93	4.863	4.22	4 110	—	—	4.11
98.40	—	—	12.75	4.553	3.08	3.682	—	—	—

TABLE II

Interfacial tension (dynes/cm.).

Saponin.	*iso*Propyl acetate.	*iso*Butyl acetate.	*n*-Butyl acetate.	*iso*Amyl acetate.
0.000 %	13.03	13.22	13.88	12.11
0.0075	8.502	11.47	9.065	9.819
0.015	7.595	9.883	7.608	7.832
0.045	6.577	6.419	5.845	5.882
0.060	5.991	5.636	5.667	5.563
0.090	5.680	5.130	4.778	5.371
0.150	5.069	4.939	4.074	4.528
0.300	4.757	4.617	3.777	4.112
0.450	3.464	4.206	3.592	4.015
0.900	3.149	3.805	3.322	3.792

ing the maximum tension, increases much more rapidly than soap concentration for dilute solutions, thereafter becomes less and ultimately any more increase in soap concentration has practically no effect on it.

TABLE III

Interfacial tension (dynes/cm.).

n-Butyl acetate. ($M \times 10^{-3}$.)	K-oleate.	K-oleate (20% free acid).	K-oleate (20% free alkali).	Na-stearate.	K-stearate.
0.000	13.88	13.88	13.88	13.88	13.88
0.233	14.00	15.25	15.70	15 80	14.88
0.4666	14.46	15.60	16.90	15.95	17.80
0.932	15.86	16.25	17.90	16.75	16.76
1.864	17 53	16.81	19.70	18.65	15.96
2.336	16.46	16.45	19.00	19 45	14.88
2.796	15.95	16.00	18.25	18.20	14.60
4.660	15.57	14.25	15.40	15.55	14.25
9.320	9.63	10.55	9.96	—	12.82

FIG. 1

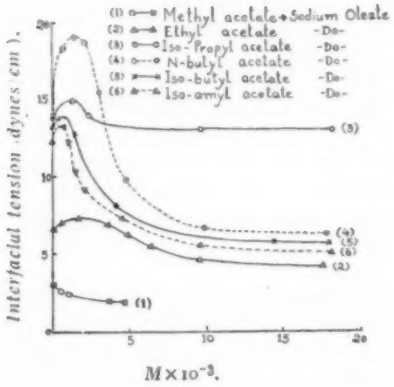
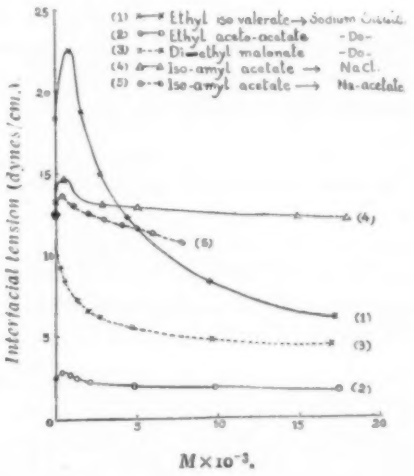


FIG. 2


(1) Ethyl iso valerate → Sodium Oleate
(2) Ethyl aceto-acetate -Do-
(3) Di-ethyl malonate -Do-
(4) Iso-amyl acetate → NaCl
(5) Iso-amyl acetate → Na-acetate
Interfacial tension (dynes/cm.).
M×10⁻³.

DISCUSSION

Initial increase in interfacial tension of alcohols and esters over the low increasing range of soap concentrations and then its usual decrease, is explained on the basis of these liquids having a ring structure as postulated by Smith and McReynolds (*J. Amer. Chem. Soc.*, 1939, **61**, 1963) and further that the reversal of electrical double

layer at the interface of aqueous medium and such a liquid takes place with the variation in soap concentration. From the data of esterification, saponification and dissociation constants, they have postulated that acids with a chain involving four or more carbon atoms have a ring structure. Further, they have stated that irregularities in optical rotatory power, noted by Pickard and Kenyon for homologous alcohol series (*J. Chem. Soc.*, 1911, **99**, 45) could be satisfactorily interpreted in the light of a ring formed through hydrogen bond and also that the ring structure through hydrogen bond may explain other anomalies, particularly the peculiar effect which the ethyl group often exerts. The effect of the nature of carbon chain on the rate of acid catalysed and base catalysed prototropy of phenylalkyl ketones (Evans and Gordon, *ibid.*, 1938, 1434) may be explained by the formation of such a ring containing four carbons as easily as by the three carbon ring. In this connection, Huggins (*J. Org. Chem.*, 1936, 407) has pointed out that in general, hydrogen bonds are more stable when the distances through which the bond operates are small. This type of ring must by its very nature be quite unstable. Liquids, referred to above, should have this type of unstable ring structure through the hydrogen bond. There is formed at the interface of such a liquid and aqueous phase an electrical double layer, as suggested by Helmholtz, Gouy and others (McBain, "Colloid Science", 1950) and correspondingly, there exists a double layer potential.

Much work has been done by Beutner, Loeb and Baur (*Z. Elektrochem.*, 1913, **19**, 509 ; 1926, **32**, 547; *Z. physikal. Chem.*, 1923, **104**, 472; *Rec. trav. chim.*, 1923, **42**, 656) on potential differences existing between organic liquids and aqueous salt solutions. The double layer potential, which is due to the preferential adsorption of one or the other ion on the liquid interface, has been found to change, when the composition of the aqueous phase is changed.

The relation between double layer potential and interfacial tension between mercury and aqueous solution was first studied by Lippmann and others (*Ann. chim. phys.*, 1875, **5**, 494; *Z. physikal. Chem.*, 1931, **154**, 454 ; *J. Phys. Chem.*, 1935, **39**, 439). With increasing applied potential, the charge on mercury decreases and is then neutralised, the interfacial tension increases while this happens, reaching a maximum, when the charge is annulled. Further increase of potential develops opposite charge on the mercury, and the tension again begins to fall.

In the present work, such a double layer potential between the organic liquid and aqueous phase is presumed to be decreased by increasing ionic atmosphere in very dilute solutions with increase in soap concentration. With the consequent lowering of charge density at the interface, it is accompanied by an increase of surface tension. When the potential of the double layer is completely annulled by the increasing ionic atmosphere, the interfacial tension will be maximum. With increasing soap concentration, however, a double layer of opposite sign to the original will be formed, and the sign of potential is now reversed ; with increase in charge density of this layer, now again the interfacial tension goes on decreasing. The development of the reversal of electrical double layer in case of esters and alcohols, referred to, should be ascribed to the unstable ring structure through the hydrogen bond. In case of other liquids, viz, butyl and

amyl alcohols, diethyl malonate and methyl acetate, there should not be H-bonding possibility, and so the reversal of double layer would not take place. Therefore, there is observed a gradual decrease of interfacial tension with increasing soap concentration over the entire range.

The work on interfacial tension variations at the interface between organic liquids, referred to, and mixed aqueous salt solutions viz., KCl-$HgCl_2$, KNO_3-$Pb(NO_3)_2$ etc. indicating complex formations between these salts, provides confirmation for this type of explanation. These results will be discussed in later papers.

In the case of *iso*amyl acetate (Fig. 2) such a behaviour is also observed with a very dilute solution of sodium acetate and sodium chloride, as in the case of colloidal electrolyte, sodium oleate. In a very dilute aqueous solution, the soap behaves like an ordinary electrolyte and is considerably ionised into an alkali metal cation and a fatty acid ion. At an appreciable concentration, however, the anions aggregate together to form ionic micelles (McBain).

With the saponin solution (Table II), however, only the decease in the interfacial tension is observed with its increasing concentration over the entire range, as it would not provide ionic atmosphere like an electrolyte.

The peak in interfacial tension is maximum with *n*-butyl acetate, ethyl *iso*valerate and *sec.*-octyl alcohol, viz., 5.5, 4.69 and 6.83 dynes/cm. respectively and minimum with hexyl alcohol, ethyl acetoacetate and ethyl acetate, viz., 0.87, 0.33 and 0.74 dynes/cm. respectively. It may be possible that the peak might be related to the degree of stability of the ring character through H-bond in these cases. Further work along these lines is in progress.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART I. $HgCl_2$—KCl—H_2O SYSTEM

BY MISS HEMLATA J. KAZI AND C. M. DESAI

Measurements of interfacial tension between *n*-butyl acetate and solutions containing KCl and $HgCl_2$ in varying proportions indicate the formation of seven complexes in solution between KCl and $HgCl_2$, viz. (1) $4KCl.\ HgCl_2$, (2) $3KCl.\ HgCl_2$, (3) $2\ KCl.\ HgCl_2$, (4) $3\ KCl.\ 2HgCl_2$, (5) $KCl.\ HgCl_2$, (6) $2KCl.\ 3HgCl_2$ and (7) $KCl.\ 2HgCl_2$.

The formation of three complexes between $HgCl_2$ and KCl in solution, namely, $KCl.\ HgCl_2$, $KCl.\ 2HgCl_2$, and $2KCl.\ HgCl_2$ has been shown by measurements of solubility, conductivity and surface tension (Tichomiroff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 731; Foote, *Amer. Chem. J.*, **35**, 236; Arcay and Marcot, *Compt. rend.*,

1939, **209**, 881). The existence of complex $K_4(HgCl_6)$ in solution has been reported by others (Benrath, *Z. anorg. Chem.*, 1908, **56**, 258; Dey, *Curr. Sci.*, 1946, **15**, 24). Tournoeux's investigations (*Ann. chim. phys.*, 1919, *ix*, **11**, 225) indicate the formation of complexes: (1) $HgCl_2$. 2KCl. H_2O (2) $HgCl_2$. KCl. 3/4 H_2O, (3) $3HgCl_2$. 2KCl. 5/3 H_2O, (4) 2 $HgCl_2$. 3KCl. 3/5 H_2O and (5) $2HgCl_2$. KCl. H_2O. The existence of $(HgCl_3)^-$ and $(HgCl_4)^{--}$ ions has been shown in solution by the study of solubility and Raman spectra (Garret, *J. Amer. Chem. Soc.*, 1939, **61**, 2744; Nayar and Saraf, this *Journal*, 1943, **20**, 312). The viscosity, refractive index and surface tension data (Nayar *et al.*, *ibid.*, 1952, **29**, 241-254) obtained by the method of monovariation reveal the formation of six complexes: (1) 4KCl. $HgCl_2$, (2) 2KCl. $HgCl_2$, (3) 3KCl. $2HgCl_2$, (4) KCl. $HgCl_2$, (5) 2KCl. $3HgCl_2$ and (6) KCl. $2HgCl_2$.

In the present investigation the method of monovariation (Nayar, *loc. cit*), which is eminently suited for the study of complexes in solution, has been adopted for interfacial tension measurements by the drop number method (Kazi and Desai this *Journal*, 1953, **30**, 209) using *n*-butyl acetate against a series of mixed solutions of $HgCl_2$ and KCl.

Experimental

The substances used were of A. R. quality (B. D. H.). The ester was further purified by treatment with sodium carbonate solution, washing with water, drying and distilling. The middle fraction was utilised for the purpose. Potassium and mercuric chlorides were further purified by repeated crystallisations from pure distilled water. $HgCl_2$ or KCl (24 c.c.) solutions were run into a glass-stoppered 100 c.c. flask from a calibrated burette. The requisite volumes of either KCl or $HgCl_2$ were then added and the mixture made up to 100 c.c. with distilled water. The results obtained by measurements of the interfacial tension of the solutions at 30° are shown graphically in Fig 1 which also gives the results with the system $HgCl_2$-NaCl-H_2O.

Discussion

Fig. 1 shows peaks corresponding to the formation of complex compounds of molecular formulae: 4 KCl. $HgCl_2$, 3 KCl. $HgCl_2$, 2 KCl.$HgCl_2$, 3KCl. $2HgCl_2$, KCl. $HgCl_2$, 2KCl. $3HgCl_2$ and KCl. 2 $HgCl_2$. The tendency for complex formation is not evident in $HgCl_2$-NaCl-H_2O system.

The authors are inclined to take the view that the formation of these complexes corresponds to

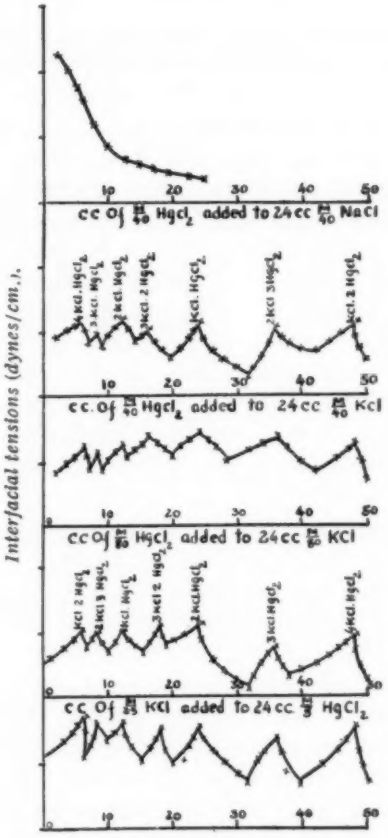
$$K_4(HgCl_6) \underset{(1)}{\rightleftarrows} \begin{cases} K_4(HgCl_6) \\ K_2(HgCl_4) \end{cases} \underset{(2)}{\rightleftarrows} K_2(HgCl_4) \underset{(3)}{\rightleftarrows} \begin{cases} K_2(HgCl_4) \\ K(HgCl_3) \end{cases} \underset{(4)}{\rightleftarrows} K(HgCl_3) \quad (5)$$

$$\begin{cases} K_2(HgCl_4) \\ 2\,HgCl_2 \end{cases} \underset{(6)}{\rightleftarrows} \begin{cases} K(HgCl_3) \\ HgCl_2 \end{cases} \quad (7)$$

sequence resulting from changes in interionic character, due to variations in electrolyte concentration. The complex 3KCl. $HgCl_2$ is interpreted in the ratio 6KCl. $2HgCl_2$

for the sequence. The complex $2KCl.\ 3HgCl_2$ is expressed as $\left\{\begin{matrix}K_2\ (HgCl_4) \\ 2\ HgCl_2\end{matrix}\right.$ and not as $\left\{\begin{matrix}2\ K\ (HgCl_3) \\ HgCl_2\end{matrix}\right.$, because in that case the interionic character would not suffer such a significant change from that of (7) as to warrant maximum tension, corresponding to the peak in the curves.

FIG. 1


Interfacial tensions (dynes/cm.).
cc of M/40 HgCl2 added to 24cc M/40 NaCl
cc of M/40 HgCl2 added to 24cc M/40 KCl
cc of M/40 HgCl2 added to 24cc M/40 KCl
cc of M/25 KCl added to 24cc M/50 HgCl2

M/25-KCl(*c.c.*) *added to* 24 *c.c. of* *M*/50-$HgCl_2$.

The method is likely to prove a very sensitive one, because it reveals the tendency of complex formation in solutions of even very low concentrations. It therefore offers an advantage in the case of sparingly soluble salts or when salts are sparingly available.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART II. THE SYSTEMS $KNO_3-Pb(NO_3)_2-H_2O$ AND $NH_4NO_3-Pb(NO_3)_2-H_2O$

By Miss Hemlata J. Kazi and C. M. Desai

Measurements of interfacial tension between *n*-butyl acetate and *sec.*-octyl alcohol against mixed solutions of KNO_3 (or NH_4NO_3) and $Pb(NO_3)_2$ indicate the formation of three compexes in the systems $KNO_3-Pb(NO_3)_2-H_2O$ and $NH_4NO_3-Pb(NO_3)_2-H_2O$ respectively.

The complex formation between $Pb(NO_3)_2$ and KNO_3 in solution has been indicated from the study of solubility and cryoscopic measurements (Le Blanc and Noyes, *Z. physikal. Chem.*, 1890, **6**, 386; Kanitz, *ibid.*, 1897, **22**, 347). Glasstone and others (*J. Chem. Soc.*, 1923, **123**, 2134; 1925, 2846) also added evidence of complex formation and indicated the probable existence of a double salt, viz. $2KNO_3.Pb(NO_3)_2$. The existence of the complex $2NH_4NO_3.Pb(NO_3)_2$ was indicated by Malquori (*Chem. Zentrl.*, 1928, II, 517 ; *Alti R. Acad. Lincei*, 1929, **9**, 231 ; *Gazzetta*, 1929, **59**, 355) from the study of conductivity and viscosity data of solutions of lead and ammonium nitrates. Recently, Nayar and Pande (*Proc. Ind. Acad. Sci.*, 1948, **27A**, 285, 353; 1949, **30A**, 251 ; this *Journal*, 1951, **28**, 112) showed by the study of viscosity, surface tension, E.M.F., transport number, magnetic susceptibility and thermometric titration measurements of mixtures of aqueous solutions of the above nitrates, the formation of complexes:

(*a*) $KNO_3.Pb(NO_3)_2$; $2KNO_3.Pb(NO_3)_2$; $4KNO_3.Pb(NO_3)_2$.

(*b*) $NH_4NO_3.Pb(NO_3)_2$; $2NH_4NO_3.Pb(NO_3)_2$; $4NH_4NO_3.Pb(NO_3)_2$.

Narasimha Murthy and others comfirmed these findings in the systems by the study of other different properties (*Proc. Ind. Acad. Sci.*, 1950, **31A**, 160; *Curr. Sci.*, 1950, **19**, 240; 1951, **20**, 13).

The interfacial tension measurements of *n*-butyl acetate against mixed aqueous solutions of mercuric chloride and potassium chloride (this *issue*, Part I, p. 287) have indicated the formation of seven complexes in solution. The present investigation deals with the study of the systems (*a*) and (*b*) studied by Nayar and others (*loc. cit.*) by the authors' method. For the procedure, *n*-butyl acetate was selected for the system (*a*), and *sec.*-octyl alcohol for (*b*) to see whether it behaved in an analogous manner to *n*-butyl acetate, as it also seems to have an unstable H-bond ring structure (cf. Miss Kazi and Desai, *Curr. Sci.*, 1952, **21**, 218).

Experimental

The method of procedure adopted in preparing solutions of the nitrates was that of Nayar and Pande (*loc. cit.*); KNO_3, NH_4NO_3 and $Pb(NO_3)_2$, pure quality (E. Merck). were further purified by repeated crystallisations from distilled water. *sec.*-Octyl alcohol (Schering-Kahlbaum) was distilled and the middle fraction was utilised for interfacial tension measurements.

Either KNO_3 or NH_4NO_3 solutions (20 c.c.) were pipetted into a flask, different volumes of $Pb(NO_3)_2$ solution were added and the mixture was made up to 60 c.c. with distilled water.

The interfacial tensions were measured by the method described earlier. The results obtained at 30° are shown graphically in Fig. 1.

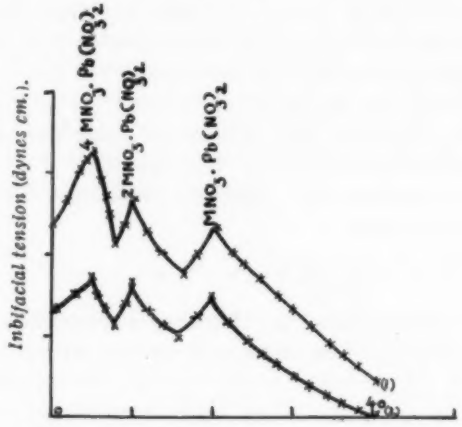
DISCUSSION

The figure shows peaks corresponding to the formation of the following complexes :

(*a*) $KNO_3.Pb(NO_3)_2$; $2KNO_3.Pb(NO_3)_2$; $4KNO_3.Pb(NO_3)_2$

(*b*) $NH_4NO_3.Pb(NO_3)_2$; $2NH_4NO_3.Pb(NO_3)_2$; $4NH_4NO_3.Pb(NO_3)_2$.

FIG. 1



M/10-$Pb(NO_3)_2$ *added in c.c. to M-10-alkalinitrate* (20 *c.c.*).

These results confirm the findings of Nayar and others (*loc. cit.*). Further, *sec*-octyl alcohol behaves as sensitively as *n*-butyl acetate in the indication of complex formation in solution.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART III. THE SYSTEM $NaNO_3$—$Pb(NO_3)_2$—H_2O

BY MISS HEMLATA J. KAZI AND C. M. DESAI

Measurements of interfacial tension between *n*-butyl acetate against a series of mixed solutions of $NaNO_3$ and $Pb(NO_3)_2$ indicate the formation of the complexes: (1) 4 $NaNO_3$. $Pb(NO_3)_2$, (2) 2$NaNO_3$. $Pb(NO_3)_2$ and (3) $NaNO_3$. $Pb(NO_3)_2$ in solution.

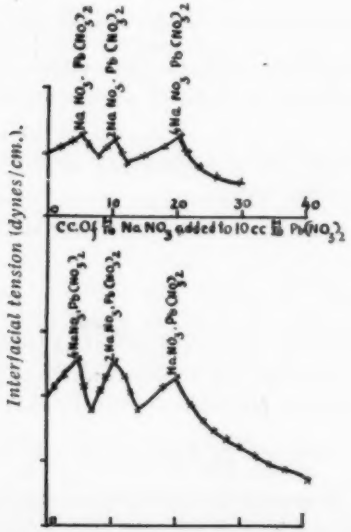
It was observed by Le Blanc and Noyes (*Z. physikal. Chem.*, 1890, **6**, 386) that solubility of $Pb(NO_3)_2$ in water at ordinary temperature was increased by the presence of KNO_3, but decreased by $NaNO_3$. The same conclusion was arrived at by Kanitz, Glasstone and others (*ibid.*, 1897, **22**, 347; *J. Chem. Soc*, 1923, **123**, 2134). The difference in the behaviour of the potassium salt from that of sodium salt was ascribed to the formation of its potassium double salt with lead nitrate in solution. Lewis and others (Dissert. Breslau, 1908; *J. Chem. Soc.* 1923, **123**, 2134; *Trans. Faraday Soc.* 1907, **2**, 199; *Z. elektrochem.*, 1904, **10**, 77; *Z. anorg. Chem.*, 1898, **17**, 327) however, observed that the addition of either KNO_3 or $NaNO_3$ to a solution of $Pb(NO_3)_2$ caused a considerable decrease in plumbous ion concentrarion, thus indicating complex formation in each case, though to a greater extent with potassium salt. The conductance, viscosity and thermometric measurements (*Proc. Ind. Acad. Sci.*, 1948, **27A** 293; this *Journal*, 1951, **28**, 112) led Nayar and Pande to conclude that no complex formation took place between $NaNO_3$ and $Pb(NO_3)_2$, but transport number measurements (*Proc. Ind. Acad. Sci.*, 1948, **27A**, 359) indicated a tendency for the formation of complex, as originally pointed out by Lewis. They, however, observed that definite complexes obeying stoichiometric laws did not seem to exist in $NaNO_3$—Pb $(NO_3)_2$—H_2O system.

The authors have examined the possibility of complex formation by the method of interfacial tension measurement.

EXPERIMENTAL

Lead nitrate and sodium nitrate (E. Merck) were recrystallised from distilled water and their stock solutions ($M/10$) were prepared in distilled water.

FIG. 1



M/10-$Pb(NO_3)_2$ added in c.c. to M/10-$NaNO_3$ (20 c.c.).

$NaNO_3$ solution (20 c.c.) was pipetted into a flask to which different volumes of $Pb(NO_3)_2$ solution were added and the total volume was made up to 60 c.c. with distilled water. In another set of experiments 10 c.c. of $Pb(NO_3)_2$ solution were taken and different volumes of $NaNO_3$ solution were added and the mixture was made up to 60 c.c.

The interfacial tensions were measured in the same manner as described in Part I (this *issue*, p. 287) at 30°. The results obtained are shown graphically in Fig. 1.

Discussion

Fig 1 shows peaks corresponding to the formation of the following complexes; $NaNO_3$. $Pb(NO_3)_2$; $2NaNO_3$. $Pb(NO_3)_2$; $4NaNO_3$. $Pb(NO_3)_2$. These results are in conformity with the conclusions (qualitative) arrived at by Lewis and others (*loc. cit*). This method of interfacial tension measurements of a liquid with unstable H-bond ring structure being extremely sensitive, opens a wide field in the investigations of the existence of complex in salt solutions, in as much as it reveals that definite complexes, obeying stoichiometric laws, also seem to exist in $NaNO_3$—$Pb(NO_3)_2$—H_2O system, just as in the case of analogous potassium and ammonium nitrate systems. The authors consider that the following equilibrium sequence exists:

$$M\,[Pb(NO_3)_3] \rightleftarrows M_2\,[Pb(NO_3)_4] \rightleftarrows M_4\,[Pb(NO_3)_6]$$

as a result of changes in the interionic character, due to variations in electrolyte concentration, where M is either potassium, ammonium or sodium in the system.

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